*Supporting Information for*

# General and Practical Potassium Methoxide/Disilane-Mediated Dehalogenative Deuteration of (Hetero)Arylhalides

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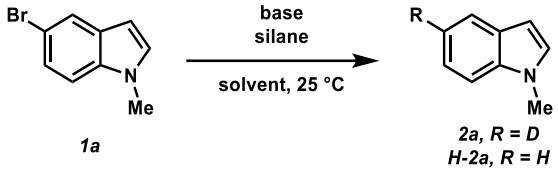
**General Information and Materials**

Unless otherwise stated, all reactions were carried out with oven-dried glassware under an atmosphere of dry argon using Schlenk manifolds. Reactions were monitored by thin-layer chromatography (TLC) or gas chromatography mass spectrometry (GC-MS). TLC was performed using Huanghai 8±0.2 μm precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, $KMnO_4$, *p*-anisaldehyde, or phosphomolybdic acid staining. Huanghai silica gel (particle size 300 – 400 or 200 – 300 mess) was used for silica gel chromatography. $^1$H NMR spectra were recorded at room temperature on a Bruker ADVANCE III 400 MHz spectrometer and were reported relative to $CDCl_3$ (δ 7.26 ppm), $CD_3OD$ (δ 4.87 ppm), or DMSO-$d_6$ (δ 2.50 ppm). $^{13}$C NMR spectra were recorded on a Bruker ADVANCE III 400 MHz spectrometer and were reported relative to $CDCl_3$ (δ 77.16 ppm), $CD_3OD$ (δ 49.00 ppm), or DMSO-$d_6$ (δ 39.52 ppm). $^2$H NMR spectra were recorded at room temperature on a Bruker ADVANCE 800 MHz spectrometer and were reported relative to $CDCl_3$ (δ 7.26 ppm). Data for $^1$H NMR were reported as chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration) using standard abbreviations for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, and br = broad signal. Data for $^{13}$C NMR were reported in terms of chemical shifts (δ ppm). GC-MS analyses were carried out on an Agilent 7890B gas chromatograph equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent) and an Agilent 5977A quadrupole mass-selective detector (MSD) in an electron ionization (EI) mode. High resolution mass spectra (HRMS) were obtained by use of Thermo Fisher Scientific LTQ FTICR-MS spectrometer, Thermo Fisher Scientific LTQ Orbitrap Elite mass spectrometer, or Bruker Compact TOF mass spectrometer in an electrospray ionization mode (ESI+) or an atmospheric pressure chemical ionization (APCI+).

Petroleum ester (60 ~ 90 $^o$C) was used as eluent for silica gel chromatography. Dry solvents were purchased commercially or were dried by passage through an activated alumina column under argon. Deuterated acetonitrile (99.8 atom% D) and reagent grade hexamethyldisilane were distilled over molecular sieves and were stored under an argon atmosphere. Other reagents were purchased commercially and used without further purification unless otherwise noted.

**Table S1. Reaction Condition Optimizations**




| | entry[a] | base | silane | solvent | time (h) | conc (mol/L) | conv (%)[b] |
|---|---|---|---|---|---|---|---|
| bases | 1 | LiOMe | $Me_3SiSiMe_3$ | MeCN | 12 | 0.2 | NR |
| | 2 | NaOMe | $Me_3SiSiMe_3$ | MeCN | 12 | 0.2 | 9 (**H-2a**) |
| | 3 | KOMe | $Me_3SiSiMe_3$ | MeCN | 5 | 0.2 | > 95 (86%[c], **H-2a**) |
| | 4 | $CsOH•H_2O$ | $Me_3SiSiMe_3$ | MeCN | 12 | 0.2 | 31 (**H-2a**) |
| | 5 | KOEt | $Me_3SiSiMe_3$ | MeCN | 12 | 0.2 | 88 (**H-2a**) |
| | 6 | KO$^t$Bu | $Me_3SiSiMe_3$ | MeCN | 12 | 0.2 | NR |
| | 7 | KOTMS | $Me_3SiSiMe_3$ | MeCN | 6 | 0.2 | > 95 (80%[c], **H-2a**) |
| | 8 | KOH | $Me_3SiSiMe_3$ | MeCN | 12 | 0.2 | 78 (**H-2a**) |
| | 9[d] | KOH | $Me_3SiSiMe_3$ | MeCN | 12 | 0.2 | > 95 (83%[c], **H-2a**) |
| | 10 | – | $Me_3SiSiMe_3$ | MeCN | 12 | 0.2 | NR |
| silanes | 11 | KOMe | – | MeCN | 12 | 0.2 | NR |
| | 12 | KOMe | $Ph_3SiSiPh_3$ | MeCN | 12 | 0.2 | 10 (**H-2a**) |
| | 13 | KOMe | $Et_3SiH$ | MeCN | 12 | 0.2 | trace |
| | 14 | KOMe | PMHS | MeCN | 12 | 0.2 | 12 (**H-2a**) |
| solvents | 15 | KOMe | $Me_3SiSiMe_3$ | THF | 12 | 0.2 | NR |
| | 16 | KOMe | $Me_3SiSiMe_3$ | $Et_2O$ | 12 | 0.2 | NR |
| | 17 | KOMe | $Me_3SiSiMe_3$ | MeOH | 12 | 0.2 | NR |
| | 18 | KOMe | $Me_3SiSiMe_3$ | $CH_2Cl_2$ | 12 | 0.2 | NR |
| | 19 | KOMe | $Me_3SiSiMe_3$ | toluene | 12 | 0.2 | NR |
| | 20 | KOMe | $Me_3SiSiMe_3$ | $^t$BuOH | 12 | 0.2 | NR |
| | 21 | KOMe | $Me_3SiSiMe_3$ | DMSO | 4 | 0.2 | > 95 (83%[c], **H-2a**) |
| concentration | 22[e] | KOMe | $Me_3SiSiMe_3$ | MeCN | 5 | 0.2 | > 95 (90, **H-2a**) |
| | 23[e] | KOMe | $Me_3SiSiMe_3$ | MeCN | 5 | 0.5 | > 95 (91%[c], **H-2a**) |
| | 24[e] | KOMe | $Me_3SiSiMe_3$ | MeCN/THF | 5 | 0.5 | 84 (**H-2a**) |
| | 25[e] | KOMe | $Me_3SiSiMe_3$ | MeCN (20 equiv) | 5 | 1.0 | > 95 (92%[c], **H-2a**) |
| | 26[e] | KOMe | $Me_3SiSiMe_3$ | MeCN (10 equiv) | 5 | 1.9 | 93 (**H-2a**) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ratio of reagents | 27[e] | KOMe | $Me_3SiSiMe_3$ (1.5 equiv) | MeCN (20 equiv) | 5 | 1.0 | > 95 (90%[c], **H-2a**) |
| | 28[e] | KOMe | $Me_3SiSiMe_3$ (1 equiv) | MeCN (20 equiv) | 5 | 1.0 | 84 (**H-2a**) |
| | 29[e] | KOMe (1.5 equiv) | $Me_3SiSiMe_3$ | MeCN (20 equiv) | 5 | 1.0 | 78 (**H-2a**) |
| | 30[e] | KOMe (1 equiv) | $Me_3SiSiMe_3$ | MeCN (20 equiv) | 5 | 1.0 | 55 (**H-2a**) |
| deuteration | 31[e] | KOMe | $Me_3SiSiMe_3$ | $CD_3CN$ (1.0 mL) | 5 | 1.0 | > 95 (94%[c], **2a**) |
| | 32[e] | KOMe | $Me_3SiSiMe_3$ | $CD_3CN$ (20 equiv) | 5 | 1.0 | > 95 (91%[c], **2a**) |
| | 33[e,f] | KOMe | $Me_3SiSiMe_3$ | $CD_3CN$ (20 equiv) | 5 | 1.0 | > 95 (87%[c], **2a**) |

[a]Reactions were conducted with 0.2 mmol of **1a**, 0.4 mmol of base and 0.4 mmol of silane in 1 mL of solvent for the indicated time, as monitored by TLC. [b]Determined by $^1$H NMR analyses. [c]Isolated yield. [d]0.8 mmol of $Me_3SiSiMe_3$ (4 equiv) was used. [e]With 0.5 mmol of **1a**. [f]The reaction was carried out using Schlenk manifold under argon. NR = no reaction. PMHS, polymethylhydrosiloxane.

***General Procedure for Condition Optimizations (Table S1)***: In an argon-filled glove box, 5-Br-*N*-methylindole **1a** (41.8 mg, 0.2 mmol), base (0.4 mmol), silane (0.4 mmol) and 1 mL of solvent were added to a screw-capped vial equipped with a magnetic stirring bar. The vial was sealed and stirred at 25 ℃ for the indicated time. Then the vial was removed from the glove box and diluted with water (10 mL). The aqueous phase was extracted with $Et_2O$ (10 mL × 3) and the combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$. The solvents were removed under reduced pressure and the conversion was determined by $^1$H NMR analysis of the crude mixture. For the examples with isolated yield, the desired product was purified by silica gel chromatography (2% ethyl acetate in petroleum ether).

**Screening of bases (entries 1 – 10)**. In the present of 2 equivalent of $Me_3SiSiMe_3$, a variety of alkali metal alkoxides and hydroxides were examined with MeCN as a solvent. Among the screened methoxide bases, KOMe gave a fully conversion of **1a** with 86% isolated yield, but LiOMe or NaOMe was much less efficient (entries 1 – 3). Hydroxides $CsOH•H_2O$ and KOH enabled the transformation with 31% and 78% conversion respectively (entries 4 and 8). In those two reactions, siloxane ($Me_3SiOSiMe_3$) was formed as detected by GC-MS. Since the formation of siloxane from hydroxide requires extra amount of disilane in comparison with alkoxides (i.e., KOMe, which forms $Me_3SiOMe$, for more information, see below proposed

mechanism section in Scheme S2), we envisioned that the yield of the reaction could be improved by increasing disilane loading. Accordingly, a fully consumption of **1a** was obtained with KOH as the base when 4 equivalent of $Me_3SiSiMe_3$ was used (entry 9). KO$^t$Bu was also examined and failed to convert the starting material (entry 6). The reaction with KOTMS also showed similar reactivity to that with KOMe (entries 7 vs 3). Considering the fact that KOMe is more readily available and cheaper than KOTMS, the further optimizations were conducted with KOMe.

**Screening of silanes (entries 11 – 14)**. A few silanes, such as hexaphenyl disilane, triethyl silane, and polymethylhydrosiloxane, were employed in combination with KOMe as the base but led to either low conversion or no reaction.

**Screening of solvents (entries 15 – 21)**. The dehalogenation was also investigated in a variety of other solvents such as THF, $Et_2O$, MeOH, $CH_2Cl_2$, toluene, $^t$BuOH, and DMSO. As shown in Table S1, no conversion was observed in most of the solvents examined except DMSO (entry 21, >95% conversion). It is worth noting that aprotic solvents containing weak acidic protons (i.e., MeCN and DMSO) are crucial to the reaction.

**Studies toward reducing the loading of MeCN and concentration effects (entries 22 – 26)**. In order to evaluate the dehalogenation in higher concentration and obtain a more accurate isolated yield, we scaled the reaction to 0.5 mmol and conducted a series of experiments. We were glad to find that the reaction occurred smoothly at a range of concentrations (from 0.2 – 1.0 mol/L, entries 22, 23, and 25) with comparable isolated yield. Further increasing concentration to 1.9 mol/L (0.5 mmol of **1a** in 260 μL MeCN, entry 26) or using mixed solvents (MeCN/THF, 0.5 mL/0.5 mL, entry 24) resulted in a slight decrease in conversion. *Please note that the concentration mentioned here refers to substrate **1a** in MeCN without accounting the volume of $Me_3SiSiMe_3$ in order to directly compare the influence of the ratio of **1a**/MeCN to the reaction.*

**Studies toward the amount of KOMe and $Me_3SiSiMe_3$ (entries 27 – 30)**. Reducing the loading of $Me_3SiSiMe_3$ from 2 equivalent to 1.5 equivalent led to similar conversion and a slight diminution in isolated yield (entries 25 vs 27). Further lowering the disilane to 1 equivalent resulted in a decreased conversion (75%, entry 28). The experiments with less

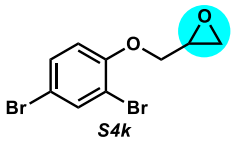
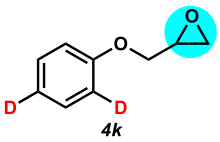
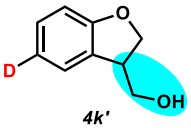
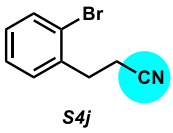
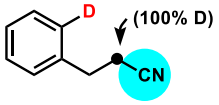
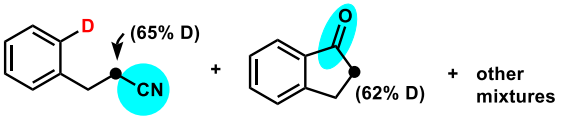
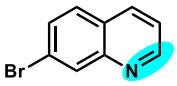
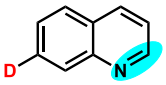
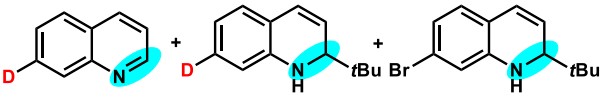
amount of KOMe (1.5 and 1 equivalent) were also investigated and much lower conversions were observed accordingly (78% and 55% respectively, entries 29 and 30).

**With $CD_3CN$ as a deuterium source (entries 31-33).** With 0.5 mmol of **1a** in 1 mL $CD_3CN$, dehalogenative deuteration reaction underwent successfully in excellent isolated yield (entry 31). When the loading of $CD_3CN$ was reduced to 20 equivalent, the desired deuterated product **2a** was isolated in a slightly lower yield (91% yield, entry 32). Furthermore, we were delighted to find that the reaction can be operated under standard Schlenk manifold without losing of reactivity (entry 33).

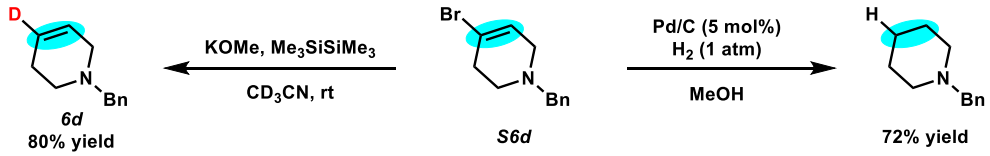
Therefore, we have identified **the optimal reaction conditions**: *KOMe (2 equiv), $Me_3SiSiMe_3$ (2 equiv), substrate (0.5 mmol), and deuterium source $CD_3CN$ (20 equiv, 520 μL) at room temperature using Schlenk techniques under argon. For arylhalides not well-dissolved in 20 equivalent of $CD_3CN$, the reactions were carried out with 1 mL of $CD_3CN$.*

## Scheme S1. Comparisons of KOMe/ Disilane-Mediated Dehalogenation with Selected Previously Reported Strategies[1,2]

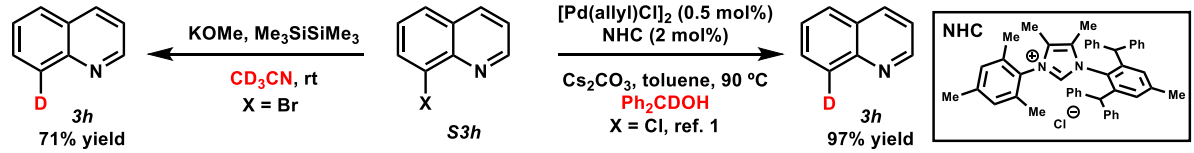
**a** KOMe/$Me_3SiSiMe_3$ Method vs Lithium-Halogen Exchange Strategy: Mild Conditions and Better Functional Group Tolerance

| substrate | *This Method*<br>conditions: KOMe (2 equiv), $Me_3SiSiMe_3$(2 equiv), $CD_3CN$, rt | *Lithium-Halogen Exchange/Quenching Strategy*<br>conditions: 1) *t*BuLi (2.2 equiv),THF, –78 °C; 2) $D_2O$ (excess) |
|---|---|---|
|  <br>*S4k* |  <br>*4k*<br>79% yield |  <br>*4k'*<br>72% yield |
|  <br>*S4j* |  <br>*4j*<br>60% yield |  <br>*4j*<br>5% yield<br>*4j'*<br>20% yield<br>+ other mixtures |
|  <br>*S3a* |  <br>*3a*<br>91% yield |  <br>*3a*<br><5% yield<br>*3a'*<br>60% yield<br>*$S_3a'$*<br>24% yield |

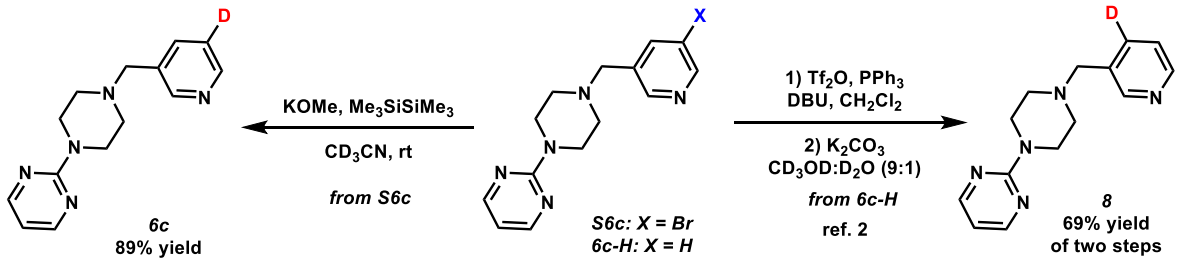
**b** KOMe/$Me_3SiSiMe_3$ Method vs Pd-Catalyzed Strategy: Better Functional Group Tolerance




**c** KOMe/$Me_3SiSiMe_3$ Method vs Pd-Catalyzed Strategy: Readily Available Reagent/Deuterium Source

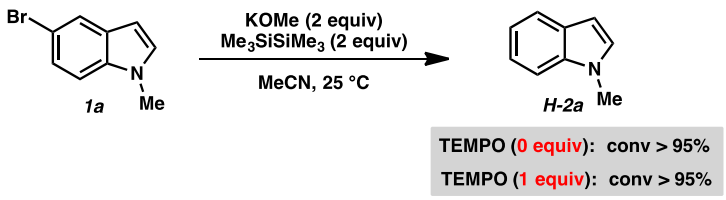



**d** KOMe/$Me_3SiSiMe_3$ Method vs Sequential Phosphorium Salt Formation/Deuteration Strategy: Complementary Selectivity



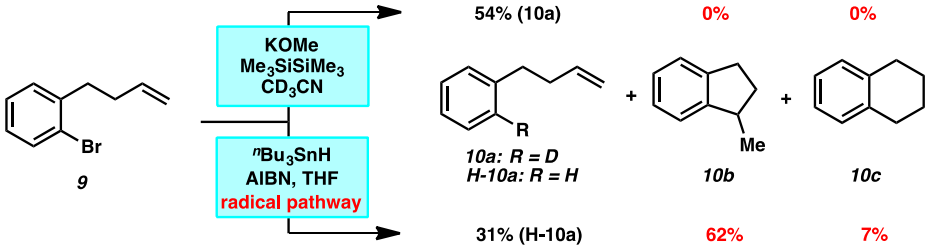
## Scheme S2. Preliminary Mechanistic Studies and Proposed Reaction Pathways

**a** Control Experiments with the Addition of TEMPO

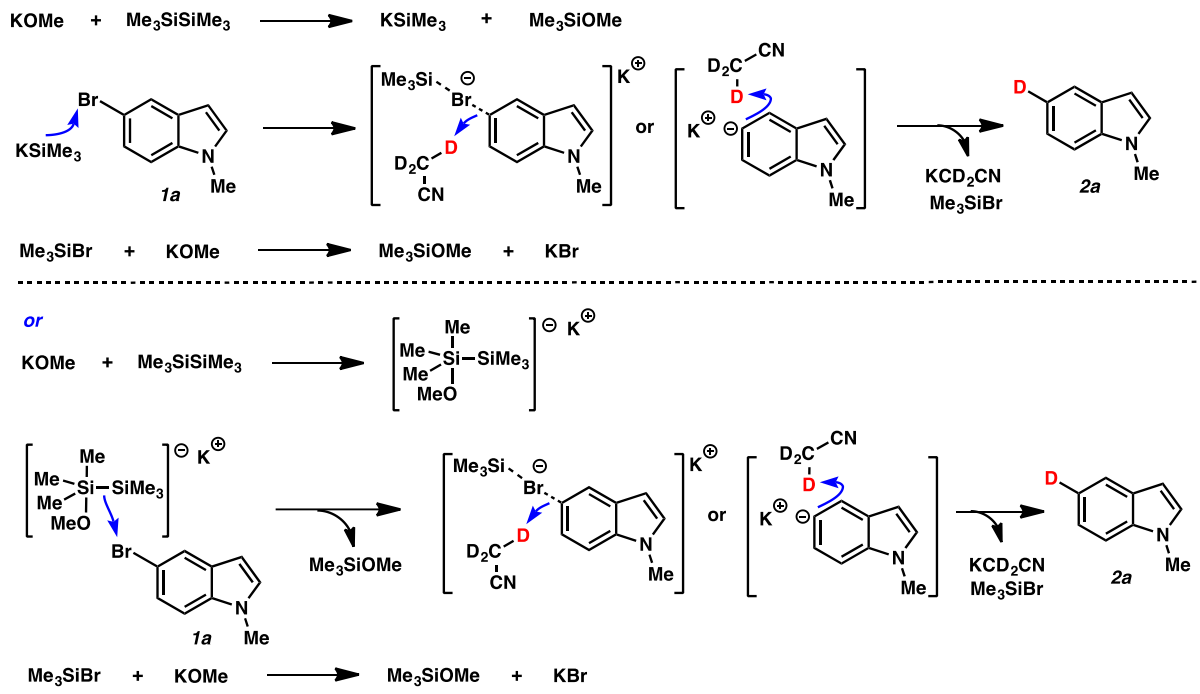



TEMPO (0 equiv): conv > 95%
TEMPO (1 equiv): conv > 95%

**b** Experiments with a Radical Probe 9



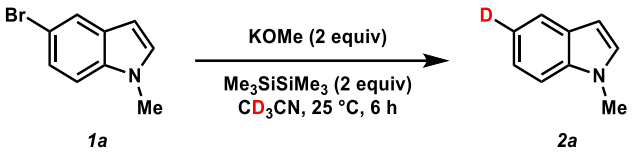

**c** Proposed Reaction Pathways



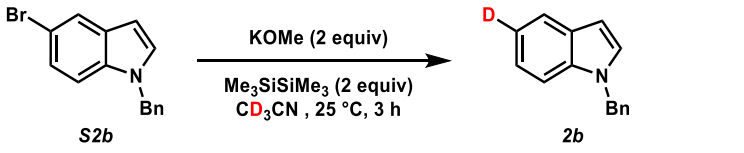

Me$_3$SiBr + KOMe → Me$_3$SiOMe + KBr

**General Procedure and Spectroscopic Data for KOMe/Disilane-Mediated Dehalogenative Deuteration of (Hetero)Arylhalides**

*Please note that the ratio of deuterium incorporation for each product was determined by integration of $^1$H NMR analysis in comparison with that of the corresponding hydrogen compound.*

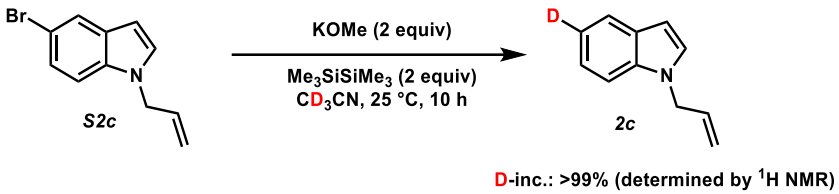



***General procedure***: To a dry Schlenk tube equipped with a magnetic stirring bar, **1a** (104.5 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol), and $CD_3CN$ (520 $\mu$L, 20 equiv) were added under argon. After stirred at 25 ℃ for 6 h, the mixture was diluted with water (10 mL), and extracted with $Et_2O$ (10 mL × 3). Then the combined organic layers were washed with brine and dried over anhydrous $Na_2SO_4$. The solvents were removed under reduced pressure and the crude mixture was purified by silica gel chromatography (2% ethyl acetate in petroleum ether) to provide 1-methyl-1*H*-indole-5-*d* (**2a)** (57.4 mg, 87% yield) as a yellow oil. $R_f$ = 0.3 (2% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.11 (d, *J* = 2.9 Hz, 1H), 6.57 (d, *J* = 2.9 Hz, 1H), 3.83 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.8, 128.9, 128.5, 121.5, 120.9, 119.1 (t, $J_{C-D}$ = 24.0 Hz), 109.3, 101.0, 33.0. HRMS (ESI+) calc'd for $C_9H_9DN$ $[M+H]^+$: 133.0871, found 133.0871.

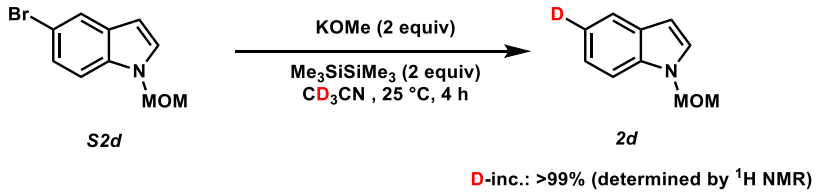



**1-Benzyl-1*H*-indole-5-*d* (2b)**: General procedure was followed. The reaction was performed with **S2b** (143.1 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 1.0 mL $CD_3CN$ (50 equiv) at 25 °C for 3 h. The desired product **2b** (95.2 mg, 92%) was obtained as a yellow oil after purification by silica gel chromatography (5% ethyl acetate in petroleum ether). $R_f$ = 0.4 (5% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, CDCl3)

δ 7.75 (s, 1H), 7.30 – 7.36 (m, 4H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.19 – 7.10 (m, 3H), 6.64 (d, *J* = 3.1 Hz, 1H), 5.32 (s, 2H). $^{13}$C NMR (100 MHz, CDCl3) δ 137.6, 136.3, 128.79, 128.75, 128.4, 127.6, 126.8, 121.7, 120.9, 119.3 (t, $J_{C\text{-}D}$ = 24.0 Hz), 109.8, 101.7, 50.1. HRMS (ESI+) calc'd for $C_{15}H_{13}DN$ $[M+H]^+$: 209.1184, found 209.1183.

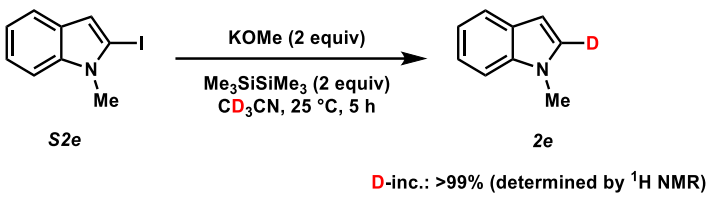



**1-Allyl-1*H*-indole-5-*d* (2c)**: General procedure was followed. The reaction was performed with **S2c** (118.1 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 μL, 1 mmol) in 520 μL $CD_3CN$ at 25 °C for 10 h. The desired product **2c** (48.2 mg, 61%, yellow oil) were obtained after purification by silica gel chromatography (5% dichloromethane in petroleum ether). $R_f$ = 0.4 (5% dichloromethane in petroleum ether); $^1$H NMR (400 MHz, CDCl3) δ 7.74 (d, *J* = 2.3 Hz, 1H), 7.41 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.30 (dd, *J* = 7.8, 2.5 Hz, 1H), 7.18 – 7.16 (m, 1H), 6.62 (s, 1H), 6.07 (ddt, *J* = 17.1, 10.3, 5.4 Hz, 1H), 5.28 (dd, *J* = 10.3, 2.1 Hz, 1H), 5.16 (dd, *J* = 17.1, 2.1 Hz, 1H), 4.85 – 4.71 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.2, 133.6, 128.7, 127.9, 121.5, 120.9, 117.4, 109.7, 101.5, 48.9. HRMS (ESI+): calc'd for $C_{11}H_{11}DN$ $[M+H]^+$: 159.1027; found: 159.1027.

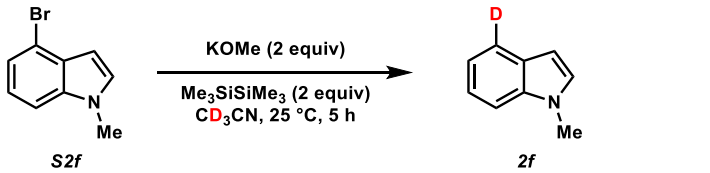



**1-(Methoxymethyl)-1*H*-indole-5-*d* (2d)**: General procedure was followed. The reaction was performed with **S2d** (120.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 μL, 1 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 4 h. The desired product **2d** (72.6 mg, 90%) was obtained as a yellow oil after purification by silica gel chromatography (5% ethyl acetate in petroleum ether). $R_f$ = 0.2 (5% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.20 (d, *J* = 3.2 Hz, 1H), 6.57 (d, *J* = 3.2 Hz, 1H), 5.47 (s, 2H), 3.26 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.5, 129.3,

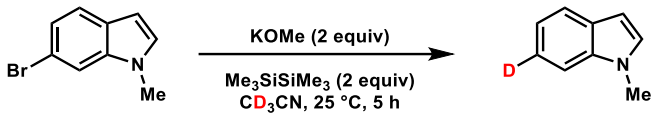
128.2, 122.2, 121.0, 110.0, 102.8, 77.6, 56.0. HRMS (ESI+): calc'd for $C_{10}H_{11}DNO$ $[M+H]^+$: 163.0976; found: 163.0976.




**1-Methyl-1*H*-indole-2-*d* (2e)**: General procedure was followed. The reaction was performed with **S2e** (129.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 5 h. The desired product **2e** (56.2 mg, 85%) was obtained as a yollow oil after purification by silica gel chromatography (1% ethyl acetate in petroleum ether). $R_f$ = 0.4 (5% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.12 (m, 1H), 6.50 (s, 1H), 3.81 (s, 3H). HRMS (ESI+) calc'd for $C_9H_9DN$ $[M+H]^+$: 133.0871, found 133.0871. These analytical data are in accordance with those reported in literature.[3]



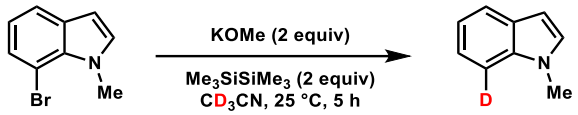

**1-Methyl-1*H*-indole-4-*d* (2f)**: General procedure was followed. The reaction was performed with **S2f** (105.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 5 h. The desired product **2f** (59.2 mg, 91%) was obtained as a yollow oil after purification by silica gel chromatography (5% ethyl acetate in petroleum ether). $R_f$ = 0.4 (5% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2, 1H), 7.34– 7.29 (m, 1H), 7.21 (d, *J* = 6.8 Hz, 1H), 7.10 (d, *J* = 2.8 Hz, 1H), 6.58 (d, *J* = 2.7 Hz, 1H), 3.83 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.8, 128.9, 128.5, 121.6, 119.2, 109.3, 100.9, 32.9. HRMS (ESI+) calc'd for $C_9H_9DN$ $[M+H]^+$: 133.0871, found 133.0878.




*S2g* *2g*

D-inc.: >99% (determined by $^1$H NMR)

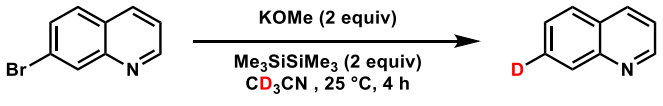
**1-Methyl-1*H*-indole-6-*d* (2g)**: General procedure was followed. The reaction was performed with **S2g** (105.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 12 h. The desired product **2g** (59.0 mg, 91%) was obtained as a yollow oil after purification by silica gel chromatography (5% ethyl acetate in petroleum ether). $R_f$ = 0.4 (5% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.39 (s, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 3.1 Hz, 1H), 6.56 (d, *J* = 3.1 Hz, 1H), 3.83 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.8, 128.9, 128.5, 121.0, 119.3, 109.2, 101.0, 33.0. HRMS (ESI+) calc'd for $C_9H_9DN$ $[M+H]^+$: 133.0871, found 133.0869.




*S2h* *2h*

D-inc.: >99% (determined by $^1$H NMR)

**1-Methyl-1*H*-indole-7-*d* (2h)**: General procedure was followed. The reaction was performed with **S2h** (105.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 5 h. The desired product **2h** (57.9 mg, 89%) was obtained as a yollow oil after purification by silica gel chromatography (5% ethyl acetate in petroleum ether). $R_f$ = 0.4 (5% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.19 – 7.10 (m, 1H), 7.08 (d, *J* = 3.1 Hz, 1H), 6.52 (d, *J* = 3.1 Hz, 1H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.7, 128.9, 128.6, 121.5, 121.0, 119.4, 101.0, 33.0. HRMS (ESI+) calc'd for $C_9H_9DN$ $[M+H]^+$: 133.0871, found 133.0874.

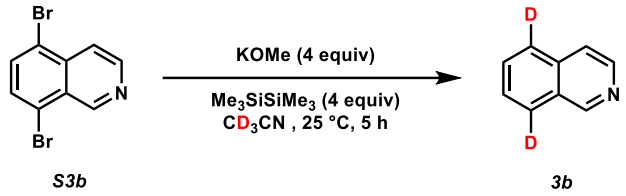



*S3a* *3a*

D-inc.: 96% (determined by $^1$H NMR)

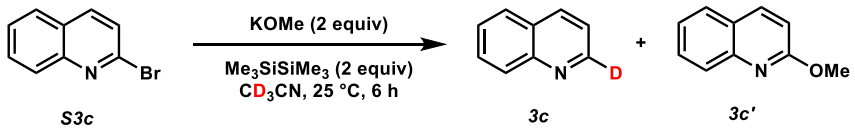
**Quinoline-7-*d* (3a)**: General procedure was followed. The reaction was performed with **S3a** (104.3 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 1.0

mL $CD_3CN$ at 25 °C for 4 h. The desired product **3a** (58.9 mg, 91%) was obtained as a yellow oil after purification by silica gel chromatography (25% ethyl acetate in petroleum ether). $R_f$ = 0.3 (25% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.24 – 8.14 (m, 1H), 8.12 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.75 – 7.71 (m, 0.04H, 96% D), 7.56 (d, *J* = 8.2 Hz, 1H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.4, 148.2, 136.5, 129.3, 128.5, 127.9, 126.7, 121.2. HRMS (ESI+): calc'd for $C_9H_7DN$ $[M+H]^+$: 131.0714; found: 131.0714.




D-inc.: 95% (determined by $^1$H NMR)

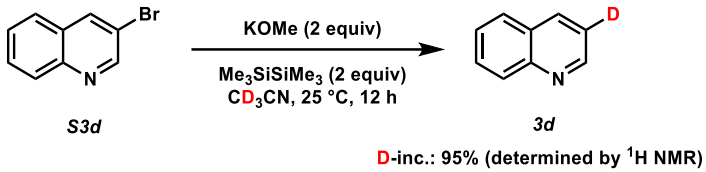
**Isoquinoline-5,8-*d*$_2$ (3b)**: General procedure was followed. The reaction was performed with **S3b** (143.5 mg, 0.5 mmol), KOMe (140.1 mg, 2 mmol), and $Me_3SiSiMe_3$ (400 μL, 2 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 5 h. The desired product **3b** (48.9 mg, 75%) was obtained as a yellow oil after purification by silica gel chromatography (20% ethyl acetate in petroleum ether). $R_f$ = 0.2 (20% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.53 (d, *J* = 5.5 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 0.05H, 95% D), 7.84 (d, *J* = 8.2 Hz, 0.05H, 95% D), 7.72 (d, *J* = 6.8 Hz, 1H), 7.68 (d, *J* = 5.7 Hz, 1H), 7.63 (d, *J* = 6.7 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.4, 142.7, 135.9, 130.6, 128.7, 127.4, 120.7. HRMS (ESI+): calc'd for $C_9H_6D_2N$ $[M+H]^+$: 132.0777; found: 132.0778.



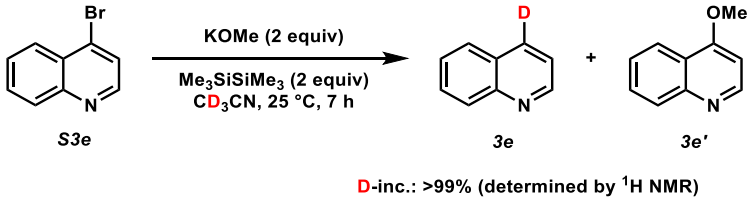

D-inc.: 97% (determined by $^1$H NMR)

**Quinoline-2-*d* (3c)**: General procedure was followed. The reaction was performed with **S3c** (104.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 μL, 1 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 6 h. The desired product **3c** (19.9 mg, 31%) and side product **3c'** (53.1 mg, 67%) were obtained after purification by silica gel chromatography. For **3c**: $R_f$ = 0.5 (30% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.2, 1.7 Hz,

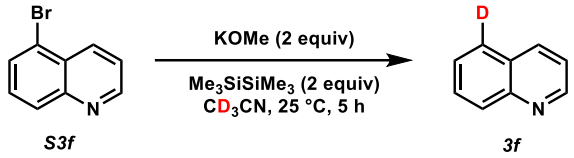
0.03H, 97%D), 8.20 (d, *J* = 8.3 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.74 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.57 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H). HRMS (ESI+): calc'd for $C_9H_7DN$ $[M+H]^+$: 131.0714; found: 131.0717. These analytical data are in accordance with those reported in literature.[4]



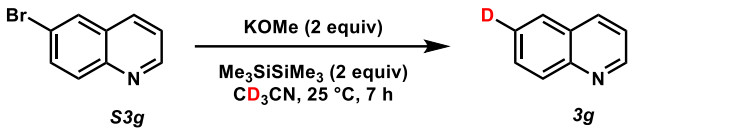

**Quinoline-3-*d* (3d)**: General procedure was followed. The reaction was performed with **S3d** (104.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **3d** (54.8 mg, 84%) was obtained as a yollow oil after purification by silica gel chromatography (5% ethyl acetate in petroleum ether). $R_f$ = 0.2 (5% ethyl acetate in petroleum ether); $^1$H NMR (600 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.20 (s, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.43 (dd, *J* = 8.2, 4.0 Hz, 0.05H, 95%D). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.2, 148.0, 136.5, 129.9, 129.3, 128.5, 128.0, 126.9. HRMS (ESI+): calc'd for $C_9H_7DN$ $[M+H]^+$: 131.0714; found: 131.0727.



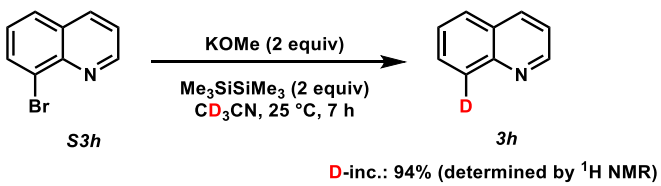

**Quinoline-4-*d* (3e)**: General procedure was followed. The reaction was performed with **S3e** (104.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 7 h. The desired product **3e** (40.2 mg, 62%) and side product **3e'** (16.7 mg, 21%) were obtained after purification by silica gel chromatography. For **3e**: $R_f$ = 0.4 (20% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 4.2 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.79 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.70 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.52 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.37 (d, *J* = 4.2 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.3, 148.0, 129.8, 129.3, 128.4, 127.9, 126.9, 121.1. HRMS (ESI+): calc'd for $C_9H_7DN$ $[M+H]^+$: 131.0714; found: 131.0722.



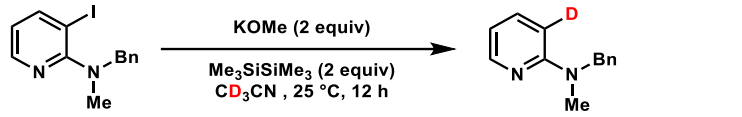

**Quinoline-5-*d* (3f)**: General procedure was followed. The reaction was performed with **S3f** (104.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 5 h. The desired product **3f** (49.5 mg, 76%) was obtained as a yollow oil after purification by silica gel chromatography (20% ethyl acetate in petroleum ether). $R_f$ = 0.4 (20% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.91 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.38 (ddd, *J* = 8.3, 1.7, 0.8 Hz, 1H), 8.06 – 8.00 (m, 1H), 7.96 (dd, *J* = 8.2, 1.2 Hz, 0.09H, 91%D), 7.77 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.62 (d, *J* = 6.4 Hz, 1H), 7.54 (dd, *J* = 8.3, 4.2 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 150.5, 147.6, 136.1, 129.6, 128.8, 127.9, 126.5, 121.5. HRMS (ESI+): calc'd for $C_9H_7DN$ $[M+H]^+$: 131.0714; found: 131.0713.




**Quinoline-6-*d* (3g)**: General procedure was followed. The reaction was performed with **S3g** (104.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 7 h. The desired product **3g** (53.0 mg, 82%) was obtained as a yollow oil after purification by silica gel chromatography (30% ethyl acetate in petroleum ether). $R_f$ = 0.4 (20% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.12 (m, 2H), 7.79 (s, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.55 – 7.49 (m, 0.04H, 96%D), 7.36 (dd, *J* = 8.3, 4.2 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.4, 148.2, 136.4, 129.6, 129.4, 128.4, 127.8, 121.2. HRMS (ESI+): calc'd for $C_9H_7DN$ $[M+H]^+$: 131.0714; found: 131.0717.



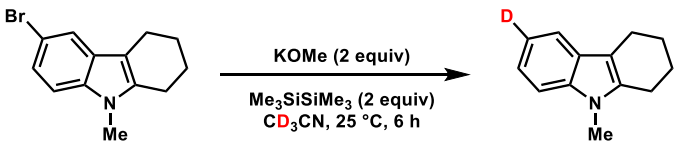
**Quinoline-8-*d* (3h)**: General procedure was followed. The reaction was performed with **S3h** (104.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 7 h. The desired product **3h** (46.2 mg, 71%) was obtained as a yollow oil after purification by silica gel chromatography (30% ethyl acetate in petroleum ether). $R_f$ = 0.5 (30% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.13 (d, *J* = 8.6 Hz, 0.06H, 94%D), 7.84 (dd, *J* = 8.2, 1.4 Hz, 1), 7.74 (dd, *J* = 6.9, 1.0 Hz, 1H), 7.57 (dd, *J* = 8.1, 6.9 Hz, 1H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H). HRMS (ESI+): calc'd for $C_9H_7DN$ $[M+H]^+$: 131.0714; found: 131.0728. These analytical data are in accordance with those reported in literature.[1]




*S4a* *4a*

D-inc.: 94% (determined by $^1$H NMR)

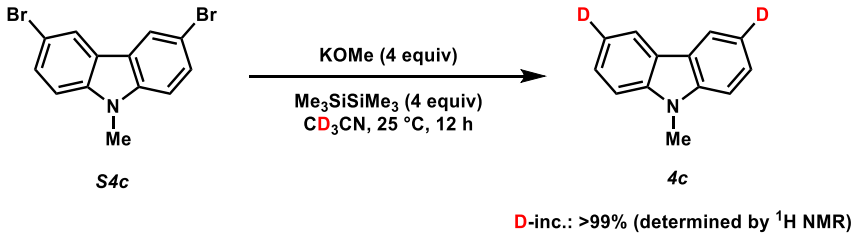
***N*-benzyl-*N*-methylpyridin-2-amine-3-*d* (4a)**: General procedure was followed. The reaction was performed with **S4a** (64.8 mg, 0.2 mmol), KOMe (28.4 mg, 0.4 mmol), and $Me_3SiSiMe_3$ (80 $\mu$L, 0.4 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **4a** (33.0 mg, 83%) was obtained as a colorless oil after purification by silica gel chromatography (10% ethyl acetate in petroleum ether). $R_f$ = 0.2 (10% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.38 (dd, *J* = 7.0, 1.7 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.20 – 7.17 (m, 3H), 6.51 (dd, *J* = 7.1, 5.0 Hz, 1H), 6.46 (d, *J* = 8.6 Hz, 0.06H, 94%D), 4.75 (s, 2H), 3.02 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.9, 147.9, 138.8, 137.4, 128.7, 127.1, 127.0, 111.9, 53.4, 36.4. HRMS (ESI+): calc'd for $C_{13}H_{14}DN_2$ $[M+H]^+$: 200.1293; found: 200.1292.




*S4b* *4b*

D-inc.: >99% (determined by $^1$H NMR)

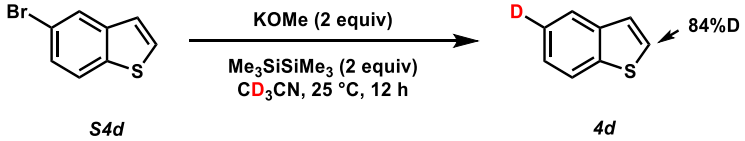
**9-Methyl-2,3,4,9-tetrahydro-1*H*-carbazole-6-*d* (4b)**: General procedure was followed except the reaction was set up in an argon-filled glovebox. The reaction was performed with **S4b** (52.6 mg, 0.2 mmol), KOMe (28.1 mg, 0.4 mmol), and $Me_3SiSiMe_3$ (80 $\mu$L, 0.4 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 6 h. The desired product **4b** (57.0 mg, 61%) was obtained as a yellow oil after purification by silica gel chromatography (10% ethyl acetate in petroleum ether). $R_f$ = 0.5 (10% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 3.61 (s, 3H), 2.72 (m, 4H), 2.00 – 1.92 (m, 2H), 1.90 – 1.83 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.8, 135.8, 127.2, 120.5, 117.7, 109.3, 108.6, 29.1, 23.38, 23.36, 22.2, 21.2. HRMS (ESI+): calc'd for $C_{13}H_{15}DN$ $[M+H]^+$: 187.1340; found: 187.1340.




*S4c* *4c*

D-inc.: >99% (determined by $^1$H NMR)

**9-Methyl-9*H*-carbazole-3,6-$d_2$ (4c)**: General procedure was followed. The reaction was performed with **S4c** (169.5 mg, 0.5 mmol), KOMe (140.1 mg, 2 mmol), and $Me_3SiSiMe_3$ (400 $\mu$L, 2 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **4c** (68.6 mg, 75%) was obtained as a white solid after purification by silica gel chromatography (10% ethyl acetate in petroleum ether). $R_f$ = 0.4 (10% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 3.87 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.0, 125.6, 122.7, 120.2, 118.6 (t, $J_{C-D}$ = 24.0 Hz), 108.4, 29.1. HRMS (ESI+): calc'd for $C_{13}H_{10}D_2N$ $[M+H]^+$: 184.1090; found: 184.1090.

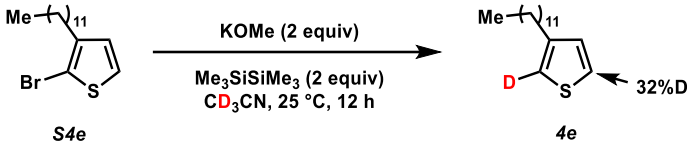



*S4d* *4d*

D-inc.: >99% (determined by $^1$H NMR)

**Benzo[*b*]thiophene-2,5-$d_2$ (4d)**: General procedure was followed. The reaction was performed with **S4d** (106.5 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol)

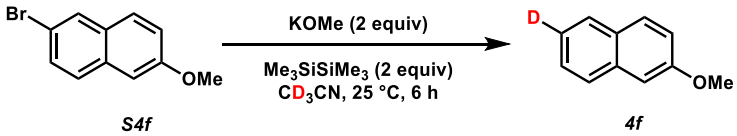
in 520 $\mu$L $CD_3CN$ at 25 °C for 12 h. The desired product **4d** (57.5 mg, 85%) was obtained as a yellow oil after purification by silica gel chromatography (100% petroleum ether). $R_f$ = 0.8 (100% petroleum ether); $^1$H NMR (400 MHz, $CD_3OD$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.80 (s, 1H), 7.50 (d, *J* = 5.4 Hz, 0.16H, 84% D), 7.36 – 7.26 (m, 2H). $^{13}$C NMR (100 MHz, $CD_3OD$) δ 141.08, 140.96, 127.3, 125.1, 124.7, 124.4, 123.3. GCMS (EI+): calc'd for $C_8H_4D_2S$ $[M]^+$: 136.03; found: 136.0.




*S4e* *4e*

D-inc.: >99% (determined by $^1$H NMR)

**3-Dodecylthiophene-2-*d* (4e)**: General procedure was followed. The reaction was performed with **S4e** (66.2 mg, 0.2 mmol), KOMe (28.4 mg, 0.4 mmol), and $Me_3SiSiMe_3$ (80 $\mu$L, 0.4 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **4e** (43.0 mg, 85%) was obtained as a yellow oil after purification by silica gel chromatography (100% petroleum ether). $R_f$ = 0.8 (100% petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 4.9 Hz, 0.68H, 32% D), 6.96 (d, *J* = 4.9 Hz, 1H), 2.67 – 2.62 (t, *J* = 7.6 Hz, 2H), 1.66 – 1.61 (m, 2H), 1.40 – 1.20 (m, 18H), 0.91 (t, *J* = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 143.3, 128.4, 125.1, 32.1, 30.7, 30.4, 29.83, 29.82, 29.80, 29.76, 29.6, 29.51, 29.50, 22.9, 14.3. HRMS (ESI+): calc'd for $C_{16}H_{28}DS$ $[M+H]^+$: 254.2047; found: 254.2047.

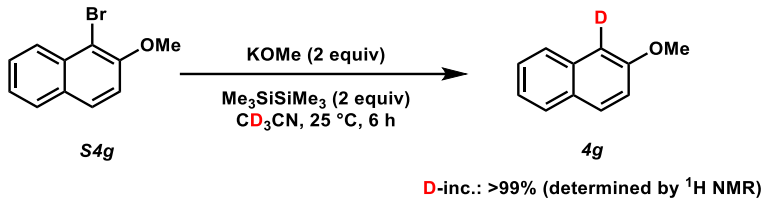



*S4f* *4f*

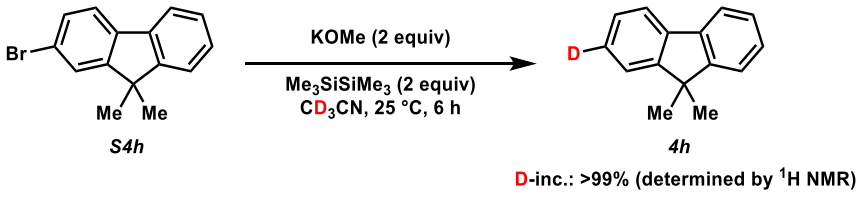
D-inc.: >99% (determined by $^1$H NMR)

**2-Methoxynaphthalene-6-*d* (4f)**: General procedure was followed. The reaction was performed with **S4f** (118.5 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 6 h. The desired product **4d** (73.3 mg, 92%) was obtained as a white solid after purification by silica gel chromatography (1% ethyl acetate in petroleum ether). $R_f$ = 0.5 (1% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.68 (m, 3H), 7.44 (d, *J* = 8.3 Hz, 1H), 7. 16 – 7.14 (m, 2H), 3.93 (s, 3H). $^{13}$C NMR

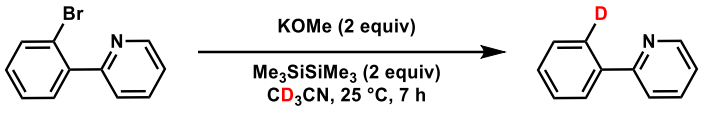
(100 MHz, $CDCl_3$) δ 157.9, 134.7, 129.5, 129.1, 127.7, 126.9, 126.4, 118.9, 105.8, 55.4. HRMS (ESI+): calc'd for $C_{11}H_{10}DO$ $[M+H]^+$: 160.0867; found: 160.0868.




**2-Methoxynaphthalene-1-*d* (4g)**: General procedure was followed. The reaction was performed with **S4g** (118.5 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 μL, 1 mmol) in 520 μL $CD_3CN$ at 25 °C for 6 h. The desired product **4g** (70.6 mg, 89%) was obtained as a white solid after purification by silica gel chromatography (1% ethyl acetate in petroleum ether). $R_f$ = 0.5 (1% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.70 (m, 3H), 7.46 – 7.42 (m, 1H), 7.37 – 7.30 (m, 1H), 7.15 (d, $J$ = 9.0 Hz, 1H), 3.93 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.6, 134.6, 129.5, 129.0, 127.8, 126.8, 126.5, 123.7, 118.9, 105.5 (t, $J_{C\text{-}D}$ = 24.0 Hz), 55.4. HRMS (ESI+): calc'd for $C_{11}H_{10}DO$ $[M+H]^+$: 160.0867; found: 160.0867.



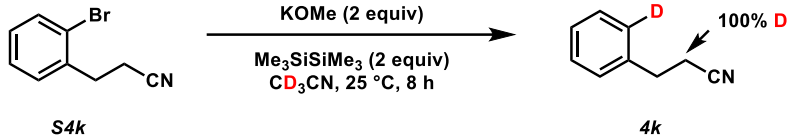

**9,9-Dimethyl-9*H*-fluorene-2-*d* (4h)**: General procedure was followed. The reaction was performed with **S4h** (136.2 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 μL, 1 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 6 h. The desired product **4h** (77.6 mg, 80%) was obtained as a white solid after purification by silica gel chromatography (100% petroleum ether). $R_f$ = 0.8 (100% petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, $J$ = 7.5 Hz, 2H), 7.50 – 7.48 (m, 2H), 7.47 – 7.33 (m, 3H), 1.57 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.7, 139.3, 127.3, 127.1, 126.9, 122.7, 122.6, 120.1, 47.0, 27.3. GCMS (EI+): calc'd for $C_{15}H_{13}D$ $[M]^+$: 195.12; found: 195.1.




*S4i* *4i*

D-inc.: >99% (determined by $^1$H NMR)

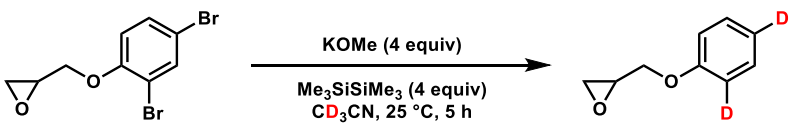
**2-(Phenyl-2-*d*)pyridine (4i)**: General procedure was followed. The reaction was performed with **S4i** (116.5 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 7 h. The desired product **4i** (66.4 mg, 82%) was obtained as a yellow oil after purification by silica gel chromatography (5% ethyl acetate in petroleum ether). $R_f$ = 0.2 (5% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.66 (m, 1H), 8.00 (m, 1H), 7.78 – 7.67 (m, 2H), 7.53 – 7.46 (m, 2H), 7.45 – 7.39 (m, 1H), 7.24 – 7.21 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.5, 149.8, 139.4, 136.9, 129.1, 128.9, 128.8, 127.0, 122.2, 120.7. GCMS (EI+): calc'd for $C_{11}H_8DN$ $[M]^+$: 156.08; found: 156.1. HRMS (ESI+): calc'd for $C_{11}H_9DN$ $[M]^+$: 157.0872; found: 157.0849.




*S4k* *4k*

D-inc.: >99% (determined by $^1$H NMR)

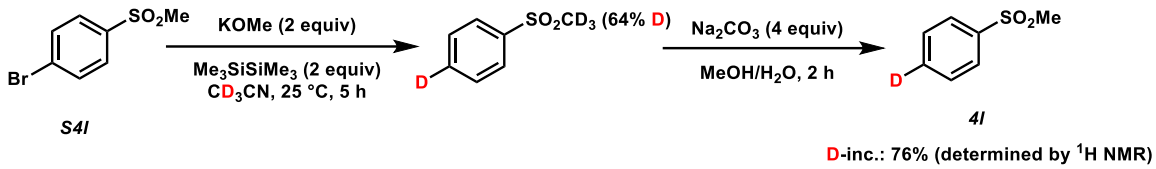
**3-(Phenyl-2-*d*)propanenitrile-2,2-$d_2$ (4j)**: General procedure was followed. The reaction was performed with **S4j** (42.0 mg, 0.2 mmol), KOMe (28.0 mg, 0.4 mmol), and $Me_3SiSiMe_3$ (80 $\mu$L, 0.4 mmol) in 210 $\mu$L $CD_3CN$ at 25 °C for 8 h. The desired product **4j** (15.8 mg, 60%) was obtained as a yellow oil after purification by silica gel chromatography (5% ethyl acetate in petroleum ether). $R_f$ = 0.3 (5% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ7.39 – 7.31 (m, 2H), 7.31 – 7.19 (m, 2H), 2.96 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.1, 129.0, 128.9, 128.4, 128.1 (t, $J_{C\text{-}D}$ = 23.9 Hz), 127.4, 119.3, 31.5, 19.0 (t, $J_{C\text{-}D}$ = 21.2 Hz). HRMS (ESI+): calc'd for $C_9H_7D_3N$ $[M+H]^+$: 135.0996; found: 135.0997.



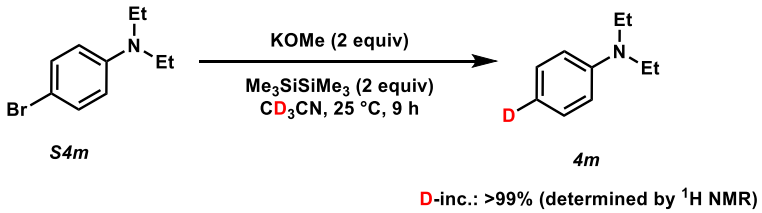

*S4k* *4k*

D-inc.: >99% (determined by $^1$H NMR)

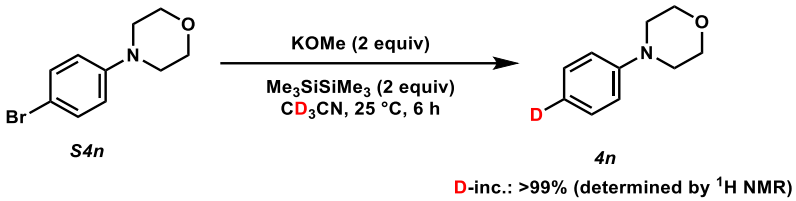
**2-((Phenoxy-2,4-*d*$_2$)methyl)oxirane (4k)**: General procedure was followed. The reaction was performed with **S4k** (154.0 mg, 0.5 mmol), KOMe (140.2 mg, 2 mmol), and $Me_3SiSiMe_3$ (400 $\mu$L, 2 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 5 h. The desired product **4k** (59.9 mg, 79%) was obtained as a yellow oil after purification by silica gel chromatography (10% ethyl acetate in petroleum ether). $R_f$ = 0.5 (10% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 6.93 (d, *J* = 8.7 Hz, 1H), 4.22 (dd, *J* = 11.0, 3.2 Hz, 1H), 3.97 (dd, *J* = 11.0, 5.6 Hz, 1H), 3.40 – 3.30 (m, 1H), 2.91 (dd, *J* = 4.8, 4.2 Hz, 1H), 2.77 (dd, *J* = 4.9, 2.7 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.6, 129.5, 129.4, 114.8, 68.8, 50.3, 44.9. HRMS (ESI+): calc'd for $C_9H_8D_2NaO_2$ [M+Na]$^+$: 175.0699; found: 175.0701.



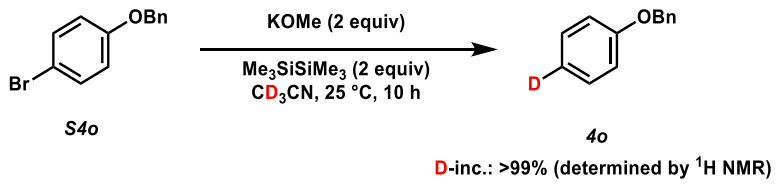

**1-((Methyl-*d*$_3$)sulfonyl)benzene-4-*d* (4l)**: General procedure was followed. The reaction was performed with **S4l** (117.5 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 5 h. The crude product was stirred with $Na_2CO_3$ (4 equiv) in 1.0 mL $H_2O$ and 1.0 mL MeOH for 2 h, then diluted with water (10 mL), and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine and dried over anhydrous $Na_2SO_4$. The desired product **4l** (65.2 mg, 83%) was obtained as a white solid after purification by silica gel chromatography (30% ethyl acetate in petroleum ether). $R_f$ = 0.3 (30% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 2H), 7.70 – 7.63 (m, 0.24H, 76% D), 7.63 – 7.54 (m, 2H), 3.06 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.7, 133.9, 129.4, 127.5, 44.6. HRMS (ESI+): calc'd for $C_7H_7DNaO_2S$ [M+Na]: 180.0200; found: 180.0202.



***N,N*-Diethylaniline-4-*d* (4m)**: General procedure was followed. The reaction was performed with **S4m** (114.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 9 h. The desired product **4m** (58.9 mg, 79%) was obtained as a yellow oil after purification by silica gel chromatography (10% ethyl acetate in petroleum ether). $R_f$ = 0.5 (10% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 8.2 Hz, 2H), 3.37 (q, *J* = 7.1 Hz, 4H), 1.18 (t, *J* = 7.1 Hz, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.9, 129.3, 112.0, 44.4, 12.7. HRMS (ESI+): calc'd for $C_{10}H_{15}DN$ $[M+H]^+$: 151.1340; found: 151.1334.

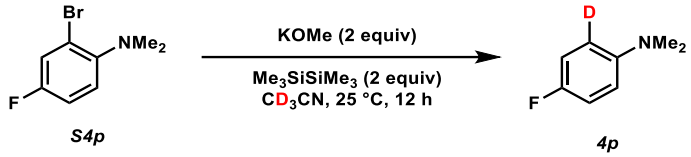



**4-(Phenyl-4-*d*)morpholine (4n)**: General procedure was followed. The reaction was performed with **S4n** (121.1 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 6 h. The desired product **4n** (65.1 mg, 79%) was obtained as a white solid after purification by silica gel chromatography (10% ethyl acetate in petroleum ether). $R_f$ = 0.3 (10% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 4.16 – 3.65 (m, 4H), 3.43 – 2.83 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.3, 129.2, 115.9, 67.0, 49.6. HRMS (ESI+): calc'd for $C_{10}H_{13}DNO$ $[M+H]^+$: 165.1133; found: 165.1127.



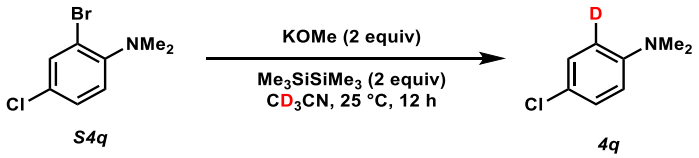

**1-(Benzyloxy)benzene-4-*d* (4o)**: General procedure was followed. The reaction was performed with **S4o** (131.6 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 10 h. The desired product **4o** (90.5 mg, 98%) was obtained as a white solid after purification by silica gel chromatography (3% ethyl acetate in petroleum ether). $R_f$ = 0.5 (3% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$)

δ 7.53 – 7.48 (m, 2H), 7.48 – 7.42 (m, 2H), 7.41 – 7.32 (m, 3H), 7.08 – 7.01 (m, 2H), 5.12 (s, 2H). HRMS (ESI+): calc'd for $C_{13}H_{12}DO$ $[M+H]^+$: 186.1024; found: 186.1024. These analytical data are in accordance with those reported in literature.[1]



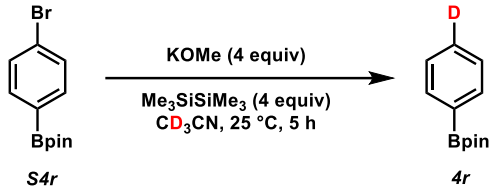

D-inc.: >99% (determined by $^1$H NMR)

**4-Fluoro-*N*,*N*-dimethylaniline-2-*d* (4p)**: General procedure was followed. The reaction was performed with **S4p** (109.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 12 h. The desired product **4p** (52.6 mg, 75%) was obtained as a yellow solid after purification by silica gel chromatography (5% ethyl acetate in petroleum ether). $R_f$ = 0.7 (5% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.05 – 6.86 (m, 2H), 6.69 (dd, $J$ = 9.7, 4.4 Hz, 1H), 2.90 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.7 (d, $J_{C\text{-}F}$ = 235.2 Hz), 147.6 (d, $J_{C\text{-}F}$ = 1.6 Hz), 115.5 (d, $J_{C\text{-}F}$ = 22.0 Hz), 115.4 (d, $J_{C\text{-}F}$ = 22.0 Hz), 114.1 (d, $J_{C\text{-}F}$ = 7.3 Hz), 113.2 (td, $J_{C\text{-}D}$ = 24.2 Hz, $J_{C\text{-}F}$ = 7.4 Hz). HRMS (ESI+): calc'd for $C_8H_{10}DFN$ $[M+H]^+$: 141.0933; found: 141.0933.

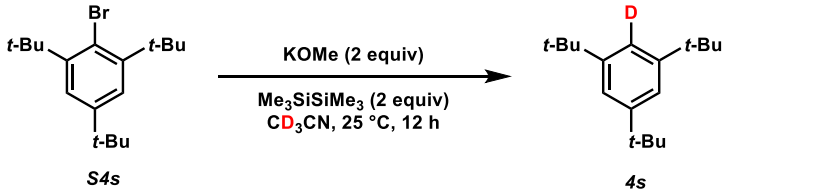



D-inc.: >99% (determined by $^1$H NMR)

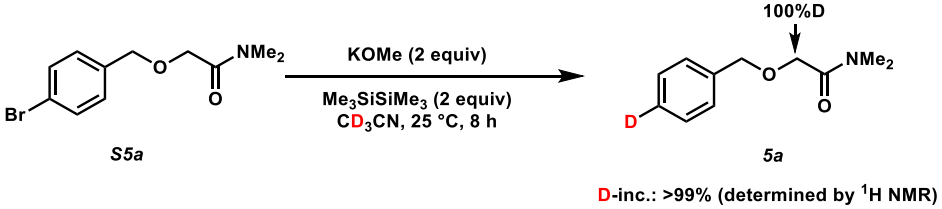
**4-Chloro-*N*,*N*-dimethylaniline-2-*d* (4q)**: General procedure was followed. The reaction was performed with **S4q** (116.5 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 12 h. The desired product **4q** (63.6 mg, 82%) was obtained as a white solid after purification by silica gel chromatography (5% ethyl acetate in petroleum ether). $R_f$ = 0.6 (5% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.13 (m, 2H), 6.66 (d, $J$ = 9.4 Hz, 1H), 2.93 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 149.1, 129.0, 128.9, 113.8, 40.9. $^2$H NMR (122 MHz, $CHCl_3$) δ 6.67 (s). HRMS (ESI+): calc'd for $C_8H_{10}DClN$ $[M+H]^+$: 157.0638; found: 157.0638.



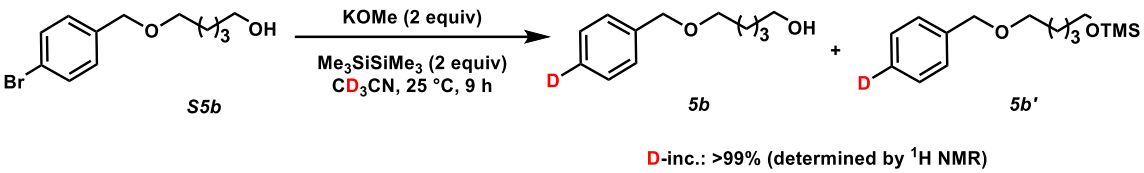

**4,4,5,5-Tetramethyl-2-(phenyl-4-*d*)-1,3,2-dioxaborolane (4r)**: General procedure was followed. The reaction was performed with **S4r** (142.0 mg, 0.5 mmol), KOMe (140.1 mg, 2 mmol), and $Me_3SiSiMe_3$ (400 $\mu$L, 2 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 5 h. *Note: the aqueous phase was extracted with dichloromethane for this reaction.* The desired product **4r** (73.8 mg, 72%) was obtained as a white solid after purification by silica gel chromatography (2% ethyl acetate in petroleum ether). $R_f$ = 0.5 (2% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.7 Hz, 2H), 1.36 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 134.9, 127.7, 83.9, 25.0. HRMS (ESI+): calc'd for $C_{12}H_{17}DBO_2$ $[M+H]^+$: 205.1493; found: 205.1494.



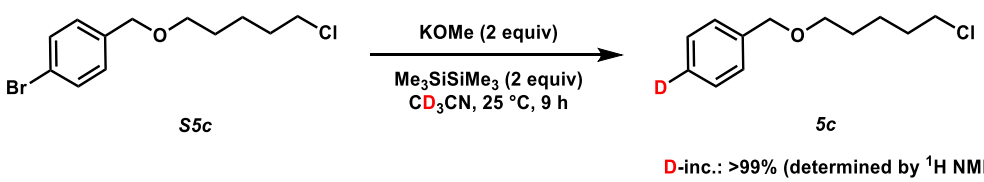

**1,3,5-Tri-tert-butylbenzene-*d* (4s)**: General procedure was followed. The reaction was performed with **S4s** (163.0 mg, 0.5 mmol), KOMe (140.1 mg, 2 mmol), and $Me_3SiSiMe_3$ (400 $\mu$L, 2 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **4s** (109.2 mg, 88%) was obtained as a white solid after purification by silica gel chromatography (100% petroleum ether). $R_f$ = 0.8 (100% petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 2H), 1.34 (s, 27H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.1, 150.0, 119.6, 35.14, 35.12, 31.7. HRMS (ESI+): calc'd for $C_{18}H_{30}D$ $[M+H]^+$: 248.2483; found: 248.2484.



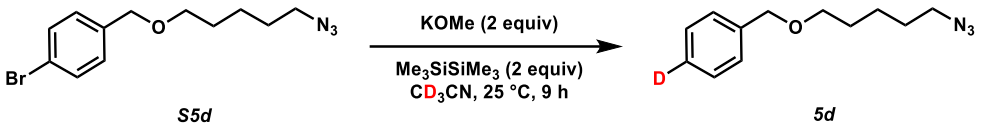
***N,N*-Dimethyl-2-((phenyl-4-*d*)methoxy)acetamide-$d_2$ (5a)**: General procedure was followed. The reaction was performed with **S5a** (135.5 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 8 h. The desired product **5a** (61.1 mg, 63%) was obtained as a white solid after purification by silica gel chromatography (50% ethyl acetate in petroleum ether). $R_f$ = 0.4 (50% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 4H), 4.61 (s, 2H), 2.98 (s, 3H), 2.96 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.3, 137.6, 128.5, 128.2, 73.2, 36.6, 35.6. HRMS (ESI+): calc'd for $C_{11}H_{12}D_3NNaO_2$ $[M+Na]^+$: 219.1183; found: 219.1189.




**Trimethyl((5-((phenyl-4-*d*)methoxy)pentyl)oxy)silane (5b)**: General procedure was followed. The reaction was performed with **S5b** (136.5 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 9 h. The desired product **5b** (74.0 mg, 76%) and silyl protected product **5b'** (23.9 mg, 18%) were obtained after purification by silica gel chromatography. For **5b**: $R_f$ = 0.4 (20% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 4H), 4.50 (s, 2H), 3.64 (t, *J* = 6.6 Hz, 2H), 3.48 (t, *J* = 6.5 Hz, 2H), 1.68 – 1.59 (m, 4H), 1.49 – 1.41 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.6, 128.4, 127.8, 73.1, 70.4, 62.9, 32.6, 29.6, 22.5. HRMS (EI+): calc'd for $C_{12}H_{18}DO_2$ $[M+H]^+$: 196.1442; found: 196.1443. For **5b'**: $R_f$ = 0.5 (5% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 4H), 4.50 (s, 2H), 3.58 (t, *J* = 6.6 Hz, 2H), 3.47 (t, *J* = 6.5 Hz, 2H), 1.74 – 1.62 (m, 2H), 1.58 – 1.54 (m, 2H), 1.48 – 1.33 (m, 2H), 0.11 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.7, 128.4, 127.8, 73.1, 70.4, 63.0, 32.6, 29.6, 22.6, 0.33. GCMS (EI+): calc'd for $C_{15}H_{25}DO_2Si$ $[M]^+$: 267.18; found: 267.1.

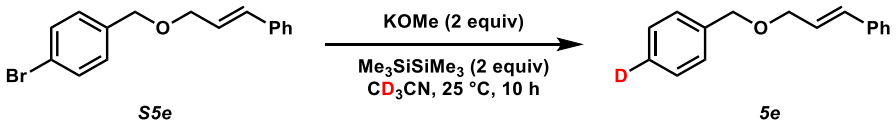


**1-(((5-Chloropentyl)oxy)methyl)benzene-4-*d* (5c)**: General procedure was followed. The reaction was performed with **S5c** (145.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 9 h. The desired product **5c** (85.5 mg, 82%) was obtained as a white solid after purification by silica gel chromatography (5% ethyl acetate in petroleum ether). $R_f$ = 0.4 (5% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $C_6D_6$) δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.29 (s, 2H), 3.17 (t, *J* = 6.2 Hz, 2H), 3.06 (t, *J* = 6.6 Hz, 2H), 1.49 – 1.31 (m, 4H), 1.32 – 1.19 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.6, 128.4, 127.8, 73.1, 70.2, 45.1, 32.6, 29.2, 23.8. HRMS (ESI+): calc'd for $C_{12}H_{17}DClO$ $[M+H]^+$: 214.1103; found: 214.1104.




D-inc.: >99% (determined by $^1$H NMR)

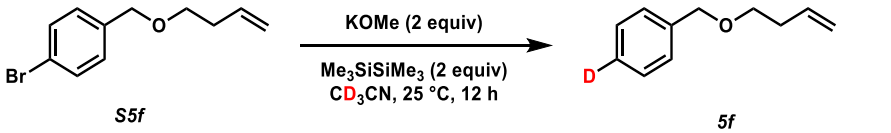
**1-(((5-Azidopentyl)oxy)methyl)benzene-4-*d* (5d)**: General procedure was followed. The reaction was performed with **S5d** (148.6 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 9 h. The desired product **5d** (99.1 mg, 91%) was obtained as a colorless oil after purification by silica gel chromatography (2% ethyl acetate in petroleum ether). $R_f$ = 0.4 (2% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 4.50 (s, 2H), 3.48 (t, *J* = 6.4 Hz, 2H), 3.27 (t, *J* = 6.9 Hz, 2H), 1.71 – 1.57 (m, 4H), 1.53 – 1.40 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.5, 128.3, 127.8, 73.0, 70.0, 51.4, 29.3, 28.7, 23.5. HRMS (ESI+) calc'd for $C_{12}H_{16}DN_3NaO$ $[M+Na]^+$: 243.1327, found 243.1325.



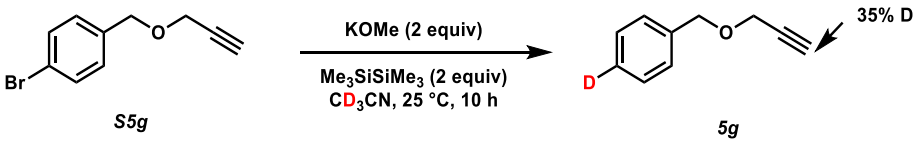

D-inc.: >99% (determined by $^1$H NMR)

**1-((Cinnamyloxy)methyl)benzene-4-*d* (5e)**: General procedure was followed. The reaction was performed with **S5e** (151.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 10 h. The desired product **5e** (98.1 mg, 88%) was obtained as a white solid after purification by silica gel chromatography (5% ethyl acetate

in petroleum ether). $R_f$ = 0.4 (5% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $C_6D_6$) δ 7.33 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.14 – 7.08 (m, 2H), 7.07 – 7.01 (m, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.20 (dt, *J* = 16.0, 5.7 Hz, 1H), 4.38 (s, 2H), 3.96 (dd, *J* = 5.7, 1.6 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.3, 136.8, 132.6, 128.7, 128.4, 127.9, 127.8, 126.6, 126.2, 72.3, 70.9. HRMS (ESI+): calc'd for $C_{16}H_{16}DO$ $[M+H]^+$: 226.1337; found: 226.1337.

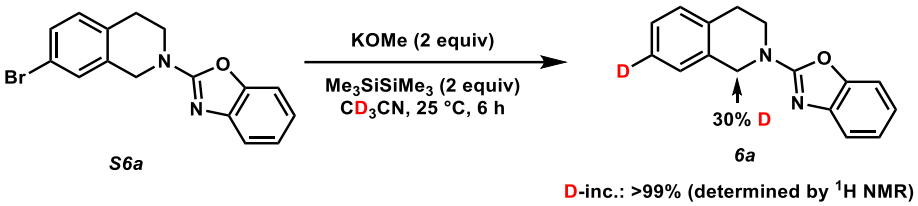



**1-((But-3-en-1-yloxy)methyl)benzene-4-*d* (5f)**: General procedure was followed. The reaction was performed with **S5f** (120.5 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 μL, 1 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **5f** (57.6 mg, 64%) was obtained as a colorless oil after purification by silica gel chromatography (1% ethyl acetate in petroleum ether). $R_f$ = 0.4 (1% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 4H), 5.85 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.22 – 4.98 (m, 2H), 4.53 (s, 2H), 3.53 (t, *J* = 6.8 Hz, 2H), 2.42 – 2.36 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.6, 135.4, 128.4, 127.8, 116.5, 73.1, 69.7, 34.4. HRMS (ESI+): calc'd for $C_{11}H_{14}DO$ $[M+H]^+$: 164.1180; found: 164.1181.

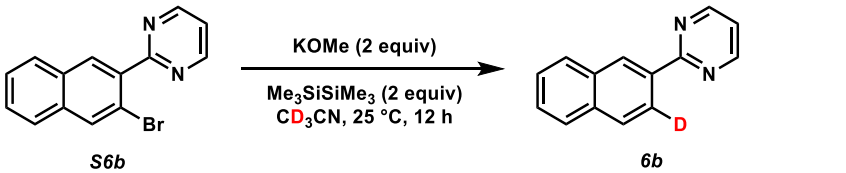



**1-((Prop-2-yn-1-yloxy)methyl)benzene-4-*d* (5g)**: General procedure was followed. The reaction was performed with **S5g** (112.5 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 μL, 1 mmol) in 520 μL $CD_3CN$ at 25 °C for 10 h. The desired product **5g** (48.7 mg, 62%) was obtained as a colorless oil after purification by silica gel chromatography (2% dichloromethane in petroleum ether). $R_f$ = 0.3 (2% dichloromethane in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 4H), 4.62 (s, 2H), 4.18 (d, *J* = 2.4 Hz, 2H), 2.47 (t, *J* =

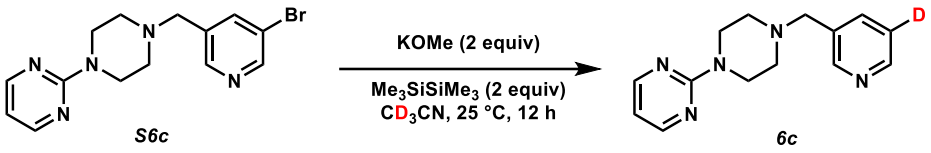
2.4 Hz, 0.65H, 35% D). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.4, 128.5, 128.3, 79.8, 74.8, 71.9, 57.2. HRMS (ESI+): calc'd for $C_{10}H_{10}DO$ $[M+H]^+$: 148.0867; found: 148.0858.



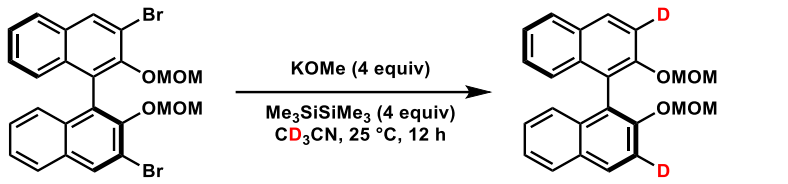

**2-(3,4-dihydroisoquinolin-2(1*H*)-yl-7-d)benzo[*d*]oxazole (6a)**: General procedure was followed. The reaction was performed with **S6a** (165.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 μL, 1 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 6 h. The desired product **6a** (100.5 mg, 80%) was obtained as a white solid after purification by silica gel chromatography (dichloromethane). $R_f$ = 0.7 (dichloromethane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.18 (m, 4H), 7.06 (td, *J* = 7.8, 1.1 Hz, 1H), 4.90 (s, 1.4H, 30% D), 4.00 (t, *J* = 5.9 Hz, 2H), 3.03 (t, *J* = 5.9 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.1, 148.9, 143.1, 134.1, 132.4, 128.9, 126.9, 126.4, 124.2, 120.7, 116.3, 108.9, 47.3, 43.2, 28.6. HRMS (ESI+): calc'd for $C_{16}H_{14}DN_2O$ $[M+H]^+$: 252.1242; found: 252.1244.



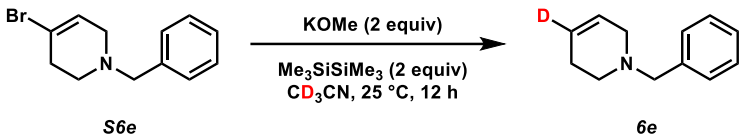

**2-(naphthalen-2-yl-3-*d*)pyrimidine (6b)**: General procedure was followed. The reaction was performed with **S6b** (56.8 mg, 0.2 mmol), KOMe (28.0 mg, 0.4 mmol), and $Me_3SiSiMe_3$ (80 μL, 0.4 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **6a** (36.0 mg, 87%) was obtained as a white solid after purification by silica gel chromatography (20% ethyl acetate in petroleum ether). $R_f$ = 0.5 (20% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.87 (d, *J* = 4.8 Hz, 2H), 8.54 (dd, *J* = 8.6, 1.7 Hz, 0.03H, 97% D), 8.02 – 8.00 (m, 1H), 7.96 (s, 1H), 7.92 – 7.85 (m, 1H), 7.60 – 7.47 (m, 2H), 7.26 – 7.20 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.8, 157.5, 134.9, 134.8, 133.4, 129.4, 128.7, 128.4, 127.9, 127.4, 126.5, 119.3. HRMS (ESI+): calc'd for $C_{14}H_{10}DN_2$ $[M+H]^+$: 208.0980; found: 208.0981.




**2-(4-((pyridin-3-yl-5-*d*)methyl)piperazin-1-yl)pyrimidine (6c)**: General procedure was followed. The reaction was performed with **S6c** (66.4 mg, 0.2 mmol), KOMe (28.0 mg, 0.4 mmol), and $Me_3SiSiMe_3$ (80 $\mu$L, 0.4 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **6c** (45.8 mg, 89%) was obtained as a yellow solid after purification by silica gel chromatography (5% methanol in dichloromethane). $R_f$ = 0.3 (5% methanol in dichloromethane); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.52 (m, 2H), 8.29 (d, *J* = 4.7 Hz, 2H), 7.73 (s, 1H), 6.48 (t, *J* = 4.7 Hz, 1H), 3.99 – 3.74 (m, 4H), 3.57 (s, 2H), 2.66 – 2.41 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 161.7, 157.9, 150.6, 148.9, 136.9, 133.3, 110.1, 60.4, 53.0, 43.6. HRMS (ESI+): calc'd for $C_{14}H_{17}DN_5$ $[M+H]^+$: 257.1619; found: 257.1621.



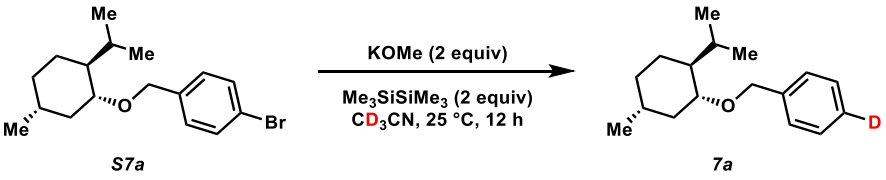

**(S)-2,2'-Bis(methoxymethoxy)-1,1'-binaphthalene-3,3'-*d*$_2$ (6d)**: General procedure was followed except the reaction was set up in an argon-filled glovebox. The reaction was performed with **S6d** (106.4 mg, 0.2 mmol), KOMe (56.2 mg, 0.8 mmol), and $Me_3SiSiMe_3$ (160 $\mu$L, 0.8 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **6d** (50.7 mg, 67%) was obtained as a white solid after purification by silica gel chromatography (5% ethyl acetate in petroleum ether). $R_f$ = 0.6 (5% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 9.0 Hz, 0.1H, 95%D) 7.37 – 7.33 (m, 2H), 7.25 – 7.20 (m, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 5.09 (d, *J* = 6.8 Hz, 2H), 4.98 (d, *J* = 6.8 Hz, 2H), 3.15 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.7, 134.1, 130.0, 129.4, 128.0, 126.4, 125.7, 124.2, 121.4, 95.3, 56.0. HRMS (ESI+): calc'd for $C_{24}H_{20}D_2NaO_4$ $[M+Na]^+$: 399.1536; found: 399.1539.




*S6e* *6e*

D-inc.: >99% (determined by $^1$H NMR)

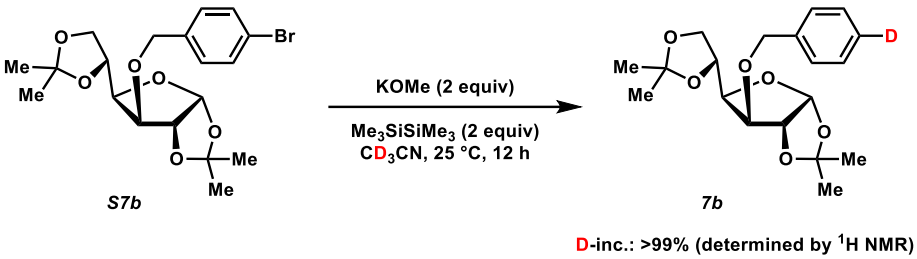
**1-Benzyl-1,2,3,6-tetrahydropyridine-4-*d* (6e)**: General procedure was followed. The reaction was performed with **S6e** (50.4 mg, 0.2 mmol), KOMe (28.0 mg, 0.4 mmol), and $Me_3SiSiMe_3$ (80 $\mu$L, 0.4 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 12 h. The desired product **6e** (27.9 mg, 80%) was obtained as a colorless oil after purification by silica gel chromatography (2% ethyl acetate in petroleum ether). $R_f$ = 0.2 (2% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 7.29 – 7.23 (m, 1H), 5.67 (s, 1H), 3.59 (s, 2H), 2.98 (q, $J$ = 3.0 Hz, 2H), 2.57 (t, $J$ = 5.7 Hz, 2H), 2.18 – 2.15 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.1, 129.4, 128.4, 127.3, 125.1, 63.0, 52.8, 49.7, 26.0. HRMS (ESI+): calc'd for $C_{12}H_{15}DN$ $[M+H]^+$: 175.1340; found: 175.1340.



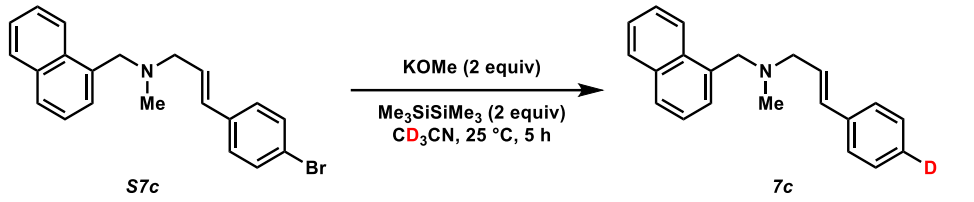

*S7a* *7a*

D-inc.: >99% (determined by $^1$H NMR)

**1-((((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl)oxy)methyl)benzene-4-*d* (7a)**: General procedure was followed. The reaction was performed with **S7a** (163.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 12 h. The desired product **7a** (117.5 mg, 95%) was obtained as a white solid after purification by silica gel chromatography (5% ethyl acetate in petroleum ether). $R_f$ = 0.4 (5% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 4H), 4.56 (d, $J_{AB}$ = 11.4 Hz, 1H), 4.30 (d, $J_{BA}$ = 11.4 Hz, 1H), 3.08 (td, $J$ = 10.6, 4.1 Hz, 1H), 2.23 (m, 1H), 2.11 (m, 1H), 1.64 – 1.47 (m, 2H), 1.35 – 1.16 (m, 2H), 0.98 – 0.71 (m, 9H), 0.63 (d, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.2, 128.3, 128.0, 78.8, 70.6, 48.4, 40.4, 34.7, 31.7, 25.6, 23.3, 22.5, 21.2, 16.2. HRMS (ESI+): calc'd for $C_{17}H_{25}DNaO$ $[M+Na]^+$: 270.1939; found: 270.1924.

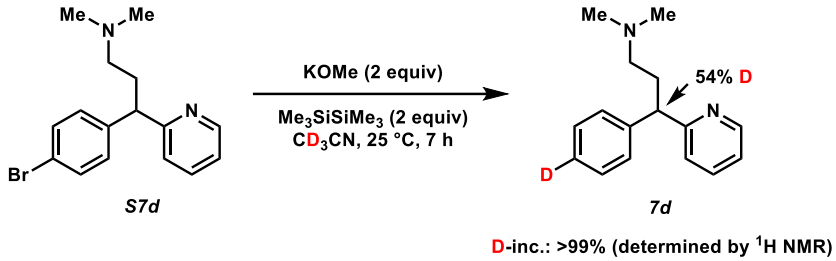



**(*3R,5R*)-5-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-((phenyl-4-d)methoxy)tetrahydrofuro[2,3-*d*][1,3]dioxole (7b)**: General procedure was followed. The reaction was performed with **S7b** (214.7 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 520 $\mu$L $CD_3CN$ at 25 °C for 12 h. The desired product **7b** (166.8 mg, 95%) was obtained as a white solid after purification by silica gel chromatography (20% ethyl acetate in petroleum ether). $R_f$ = 0.4 (20% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 4H), 5.90 (d, $J$ = 3.7 Hz, 1H), 4.69 (d, $J_{AB}$ = 11.8 Hz, 1H), 4.64 (d, $J_{BA}$ = 11.8 Hz, 1H), 4.59 (d, $J$ = 3.7 Hz, 1H), 4.38 (m, 1H), 4.14 (m, 2H), 4.05 – 3.96 (m, 2H), 1.50 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.31 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.8, 128.5, 127.8, 112.0, 109.1, 105.4, 82.8, 81.8, 81.5, 72.7, 72.5, 67.5, 27.0, 26.9, 26.4, 25.6. HRMS (ESI+): calc'd for $C_{19}H_{25}DNaO_6$ $[M+Na]^+$: 374.1684; found: 374.1685.

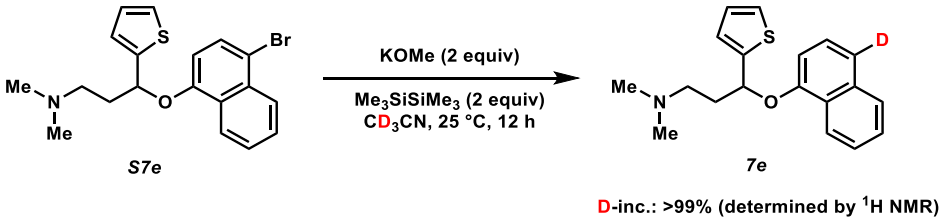



**(*E*)-*N*-Methyl-*N*-(naphthalen-1-ylmethyl)-3-(phenyl-4-*d*)prop-2-en-1-amine (7c)**: General procedure was followed. The reaction was performed with **S7c** (182.4 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 5 h. The desired product **7c** (105.4 mg, 73%) was obtained as a white solid after purification by silica gel chromatography (20% ethyl acetate in petroleum ether). $R_f$ = 0.5 (20% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, $J$ = 8.3 Hz, 1H), 7.87 (d, $J$ = 8.3, 1H), 7.80 (d, $J$ = 7.9 Hz, 1H), 7.60 – 7.38 (m, 6H), 7.34 (d, $J$ = 8.1 Hz, 2H), 6.61 (d, $J$ = 15.9 Hz, 1H), 6.41 (dt, $J$ = 15.9, 6.7 Hz, 1H), 3.98 (s, 2H), 3.31 (dd, $J$ = 6.7, 1.0 Hz, 2H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.2, 134.8, 134.0, 132.9, 132.6, 128.6, 128.1, 127.7, 127.5,

126.5, 126.1, 125.7, 125.3, 124.7, 60.5, 60.1, 42.5. HRMS (ESI+): calc'd for $C_{21}H_{21}DN$ $[M+H]^+$: 289.1810; found: 289.1810.

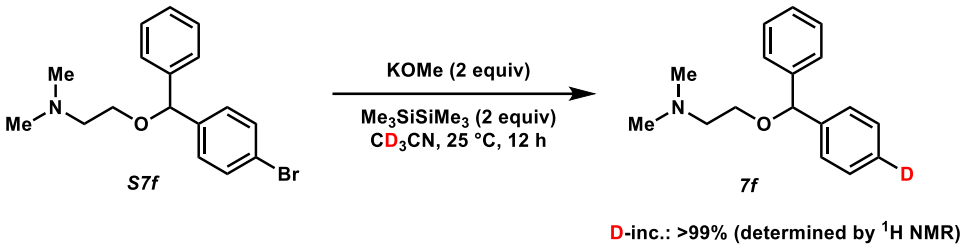



***N,N*-dimethyl-3-(phenyl-4-*d*)-3-(pyridin-2-yl)propan-1-amine-3-*d* (7d)**: General procedure was followed. The reaction was performed with **S7d** (159.0 mg, 0.5 mmol), KOMe (70.1 mg, 1 mmol), and $Me_3SiSiMe_3$ (200 $\mu$L, 1 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 7 h. The desired product **7d** (89.0 mg, 74%) was obtained as a yellow solid after purification by silica gel chromatography (10% methanol in dichloromethane). $R_f$ = 0.6 (10% methanol in dichloromethane); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.47 (m, 1H), 7.44 (td, *J* = 7.7, 1.9 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.22 – 7.16 (m, 2H), 7.11 – 7.05 (m, 1H), 6.97 (m, 1H), 4.31 – 3.71 (m, 0.46H, 54% D), 2.44 – 2.30 (m, 1H), 2.23 – 2.04 (m, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.5, 149.3, 143.6, 136.6, 128.6, 128.1, 123.0, 121.5, 57.8, 51.4, 45.4, 32.6, 32.5. HRMS (ESI+): calc'd for $C_{16}H_{19}D_2N_2$ $[M+H]^+$: 243.1825; found: 243.1822.

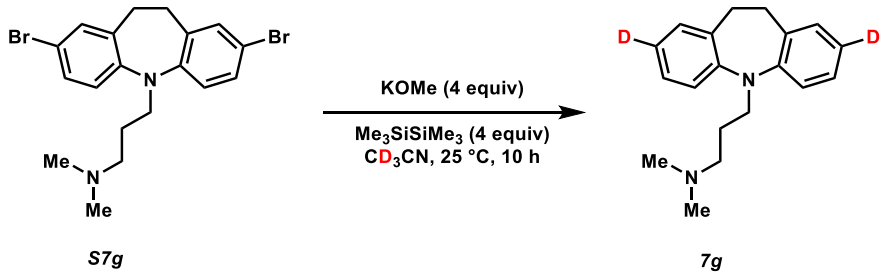



***N,N*-Dimethyl-3-((naphthalen-1-yl-4-*d*)oxy)-3-(thiophen-2-yl)propan-1-amine (7e)**: General procedure was followed. The reaction was performed with **S7e** (38.9 mg, 0.1 mmol), KOMe (14.2 mg, 0.2 mmol), and $Me_3SiSiMe_3$ (40 $\mu$L, 0.2 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **7e** (24.6 mg, 79%) was obtained as a white solid after purification by silica gel chromatography (10% methanol in dichloromethane). $R_f$ = 0.4 (10% methanol in dichloromethane); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 6.9, 2.8 Hz, 1H), 7.78 (dd, *J* = 6.6, 2.8 Hz, 1H), 7.54 – 7.42 (m, 2H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 5.0 Hz, 1H), 7.07

(d, *J* = 3.4 Hz, 1H), 6.95 – 6.93 (m, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 5.80 – 5.75 (m, 1H), 2.62 – 2.52 (m, 2H), 2.52 – 2.40 (m, 1H), 2.29 (s, 6H), 2.27 – 2.19 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.5, 145.2, 134.6, 127.6, 126.7, 126.4, 126.2, 125.8, 125.4, 124.9, 124.8, 122.2, 107.1, 74.7, 55.8, 45.5, 36.8. HRMS (ESI+): calc'd for $C_{19}H_{21}DNOS$ $[M+H]^+$: 313.1479; found: 313.1477.

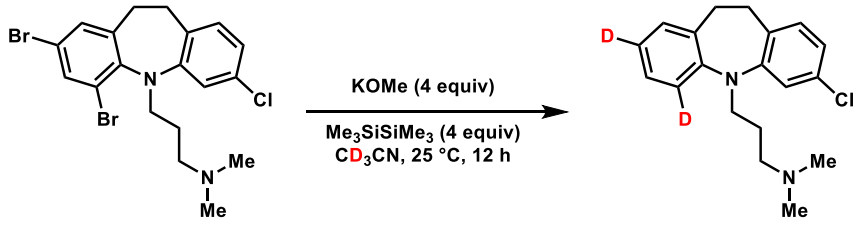



***N,N*-dimethyl-2-(phenyl(phenyl-4-*d*)methoxy)ethan-1-amine (7f)**: General procedure was followed. The reaction was performed with **S7f** (66.6 mg, 0.2 mmol), KOMe (28.0 mg, 0.4 mmol), and $Me_3SiSiMe_3$ (80 $\mu$L, 0.4 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **7f** (46.4 mg, 91%) was obtained as a yellow oil after purification by silica gel chromatography (5% methanol in dichloromethane). $R_f$ = 0.3 (5% methanol in dichloromethane); $^1$H NMR (400 MHz, $CDCl_3$) δ7.38 – 7.28 (m, 8H), 7.25 – 7.20 (m, 1H), 5.37 (s, 1H), 3.59 (t, *J* = 5.9 Hz, 2H), 2.65 (t, *J* = 5.9 Hz, 2H), 2.31 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.3, 128.5, 128.4, 127.6, 127.1, 84.2, 67.3, 58.9, 45.9. HRMS (ESI+): calc'd for $C_{17}H_{21}DNO$ $[M+H]^+$: 257.1759; found: 257.1760.




**3-(10,11-dihydro-5*H*-dibenzo[*b,f*]azepin-5-yl-2,8-$d_2$)-N,N-dimethylpropan-1-amine (7g)**: General procedure was followed. The reaction was performed with **S7g** (43.5 mg, 0.1 mmol), KOMe (28.0 mg, 0.4 mmol), and $Me_3SiSiMe_3$ (80 $\mu$L, 0.4 mmol) in 1.0 mL $CD_3CN$ at 25 °C

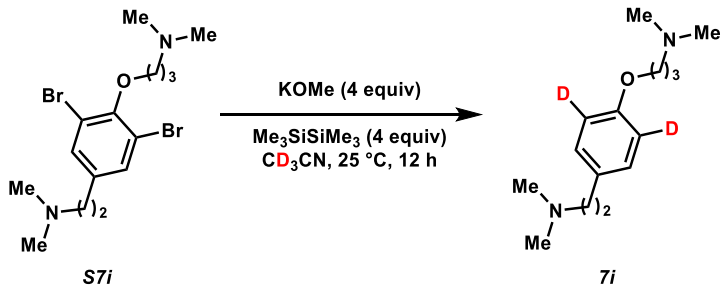
for 10 h. The desired product **7g** (22.3 mg, 79%) was obtained as a yellow oil after purification by silica gel chromatography (10% methanol in dichloromethane). $R_f$ = 0.4 (10% methanol in dichloromethane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.04 (m, 6H), 3.78 (t, *J* = 7.5 Hz, 2H), 3.16 (s, 4H), 2.44 (t, *J* = 7.5 Hz, 2H), 2.23 (s, 6H), 1.86 – 1.72 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.2, 134.3, 129.9, 126.4, 122.4 (t, $J_{C–D}$ = 26.2 Hz), 120.0, 57.5, 48.6, 45.0, 32.3, 25.5. HRMS (ESI+): calc'd for $C_{19}H_{23}D_2N_2$ $[M+H]^+$: 283.2138; found: 283.2146.




*S7h* *7h*

D-inc.: >99% (determined by $^1$H NMR)

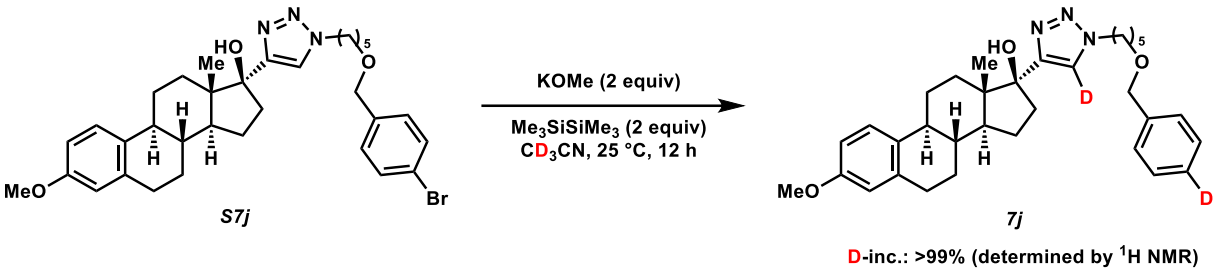
**3-(3-chloro-10,11-dihydro-5*H*-dibenzo[*b,f*]azepin-5-yl-6,8-*d*2)-N,N-dimethylpropan-1-amine (7h)**: General procedure was followed. The reaction was performed with **S7h** (94 mg, 0.2 mmol), KOMe (56.0 mg, 0.8 mmol), and $Me_3SiSiMe_3$ (160 $\mu$L, 0.8 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **7h** (57.7 mg, 91%) was obtained as a yellow oil after purification by silica gel chromatography (5% methanol in dichloromethane). $R_f$ = 0.3 (5% methanol in dichloromethane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.04 (m, 4H), 6.98 (s, 1H), 3.74 (t, *J* = 6.9 Hz, 2H), 3.19 – 3.02 (m, 4H), 2.30 (t, *J* = 7.4 Hz, 2H), 2.16 (s, 6H), 1.80 – 1.65 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 149.2, 148.0, 135.2, 131.7 131.6, 131.2, 129.4, 126.6, 120.7, 120.0, 57.7, 49.0, 45.6, 32.3, 31.6, 26.2. $^2$H NMR (122 MHz, $CHCl_3$) δ 6.96(s, 1D), 6.85(s, 1D). HRMS (ESI+): calc'd for $C_{19}H_{22}ClD_2N_2$ $[M+H]^+$: 317.1748; found: 317.1746.



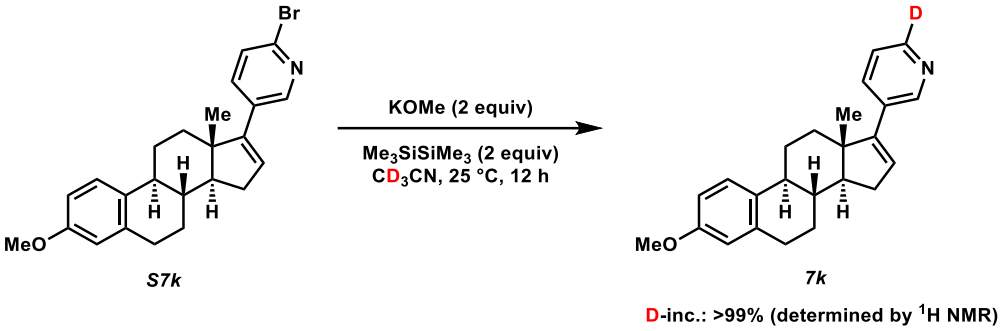

*S7i* *7i*

D-inc.: >99% (determined by $^1$H NMR)

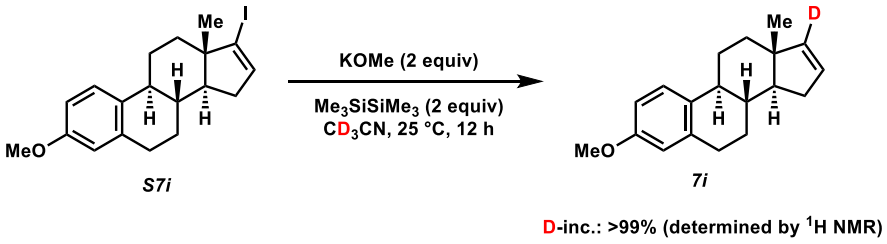
**Deuterated aplysamine-1 (7i)**: General procedure was followed. The reaction was performed with **S7i** (51.2 mg, 0.14 mmol), KOMe (39.3 mg, 0.56 mmol), and $Me_3SiSiMe_3$ (112 $\mu$L, 0.56 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **7i** (27.6 mg, 83%) was obtained as a yellow oil after purification by silica gel chromatography (10% methanol in dichloromethane). $R_f$ = 0.2 (10% methanol in dichloromethane); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 2H), 3.97 (t, *J* = 6.4 Hz, 2H), 2.74 – 2.70 (m, 2H), 2.56 – 2.40 (m, 4H), 2.29 (s, 6H), 2.26 (s, 6H), 2.01 – 1.90 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.3, 132.2, 129.5, 114.3 (t, $J_{C-D}$ = 24.1 Hz), 66.2, 61.9, 56.5, 45.6, 45.5, 33.5, 27.6. HRMS (ESI+): calc'd for $C_{15}H_{25}D_2N_2O$ $[M+H]^+$: 253.2243; found: 253.2244.




**(8*R*,9*S*,13*S*,14*S*,17*S*)-3-methoxy-13-methyl-17-(1-(((phenyl-4-*d*)methoxy)methyl)-1*H*-1,2,3-triazol-4-yl-5-*d*)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol (7j)**: General procedure was followed. The reaction was performed with **S7j** (61.5 mg, 0.1 mmol), KOMe (14.0 mg, 0.2 mmol), and $Me_3SiSiMe_3$ (40 $\mu$L, 0.2 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **7j** (43.8 mg, 82%) was obtained as a yellow solid after purification by silica gel chromatography (30% ethyl acetate in petroleum ether). $R_f$ = 0.1 (30% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 4H), 7.11 (d, *J* = 8.6 Hz, 1H), 6.67 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.61 (d, *J* = 2.6 Hz, 1H), 4.47 (s, 3H), 4.37 (t, *J* = 6.9 Hz, 2H), 3.76 (s, 3H), 3.46 (t, *J* = 6.2 Hz, 2H), 2.87 – 2.83 (m, 2H), 2.38 – 2.33 (m, 1H), 2.16 – 2.14 (m, 2H), 1.97 – 1.91 (m, 5H), 1.68 – 1.62 (m, 4H), 1.58 – 1.32 (m, 5H), 1.04 (s, 3H), 0.77 – 0.57 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.5, 153.5, 138.5, 138.1, 132.7, 128.4, 127.8, 126.4, 113.9, 111.6, 82.4, 73.1, 70.0, 55.3, 50.5, 48.7, 47.5, 43.5, 39.6, 38.1, 33.1, 30.2, 30.0, 29.2, 27.5, 26.4, 23.50, 23.48, 14.4. HRMS (ESI+): calc'd for $C_{33}H_{41}D_2N_3NaO_3$ $[M+ Na]^+$: 554.3322; found: 554.3332.

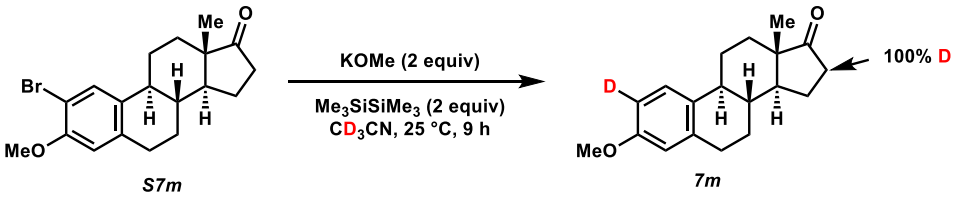



**3-((8*S*,9*S*,13*S*,14*S*)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)pyridine-6-*d* (7k)**: General procedure was followed. The reaction was performed with **S7k** (42.3 mg, 0.1mmol), KOMe (14.0 mg, 0.2 mmol), and $Me_3SiSiMe_3$ (40 $\mu$L, 0.2 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **7k** (25.7 mg, 74%) was obtained as a white solid after purification by silica gel chromatography (2% ethyl acetate in petroleum ether). $R_f$ = 0.1 (2% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.77 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.66 (d, *J* = 2.7 Hz, 1H), 6.07 (dd, *J* = 3.2, 1.7 Hz, 1H), 3.78 (s, 3H), 3.16 – 2.64 (m, 2H), 2.43 – 2.26 (m, 3H), 2.17 – 2.14 (m, 2H), 2.02 – 1.93 (m, 1H), 1.82 (td, *J* = 11.4, 6.5 Hz, 1H), 1.75 – 1.59 (m, 3H), 1.56 – 1.42 (m, 1H), 1.05 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.6, 151.5, 146.7, 138.1, 134.9, 133.7, 132.7, 130.2, 126.2, 123.5, 114.0, 111.6, 56.8, 55.4, 47.9, 44.1, 37.4, 35.4, 31.7, 29.8, 27.8, 26.6, 16.8. HRMS (ESI+): calc'd for $C_{24}H_{27}DNO$ $[M+H]^+$: 347.2228; found: 347.2234.



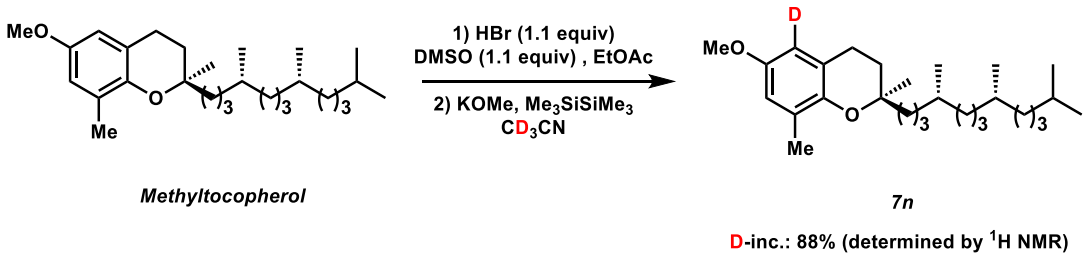

***(8S,9S,13R,14S)*-3-Methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-cyclopenta[*a*]phenanthrene-17-*d* (7i)**: General procedure was followed. The reaction was performed with **S7i** (78.8 mg, 0.2 mmol), KOMe (28.0 mg, 0.4 mmol), and $Me_3SiSiMe_3$ (80 $\mu$L, 0.4 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 12 h. The desired product **7i** (45.8 mg, 85%) was obtained as a white solid after purification by silica gel chromatography (2% ethyl acetate in petroleum ether). $R_f$ = 0.4 (2% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$)

δ 7.20 (d, *J* = 8.5 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.64 (d, *J* = 2.7 Hz, 1H), 5.74 (dd, *J* = 2.8, 1.4 Hz, 1H), 3.78 (s, 3H), 2.99 – 2.74 (m, 2H), 2.26 (m, 3H), 2.09 – 1.79 (m, 3H), 1.70 – 1.58 (m, 3H), 1.53 – 1.37 (m, 2H), 0.79 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.5, 138.1, 133.3, 129.3, 126.2, 113.9, 111.5, 55.5, 55.3, 45.8, 44.7, 37.5, 36.0, 31.9, 29.9, 28.1, 26.8, 17.2. HRMS (ESI+): calc'd for $C_{19}H_{24}DO$ $[M+H]^+$: 270.1963; found: 270.1963.




***(8R,9S,13S,14S)*-3-Methoxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-cyclopenta[*a*]phenanthren-17-one-2-*d* (7m)**: General procedure was followed. The reaction was performed with **S7m** (72.8 mg, 0.2 mmol), KOMe (28.0 mg, 0.4 mmol), and $Me_3SiSiMe_3$ (80 $\mu$L, 0.4 mmol) in 1.0 mL $CD_3CN$ at 25 °C for 9 h. The desired product **7m** (39.3 mg, 68%) was obtained as a white solid after purification by silica gel chromatography (20% ethyl acetate in petroleum ether). $R_f$ = 0.5 (20% ethyl acetate in petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 1H), 6.65 (s, 1H), 3.78 (s, 3H), 2.92 – 2.89 (m, 2H), 2.42 – 2.40 (m, 1H), 2.28 – 2.24 (m, 1H), 2.11 – 1.88 (m, 3H), 1.67 – 1.38 (m, 6H), 0.91 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.7, 137.9, 132.2, 126.4, 114.1, 55.4, 50.5, 48.2, 44.1, 38.5, 31.7, 29.8, 26.7, 26.1, 21.5, 14.0. MS (ESI+): calc'd for $C_{19}H_{22}D_3O_2$ $[M+H]^+$: 288.20; found: 288.2.

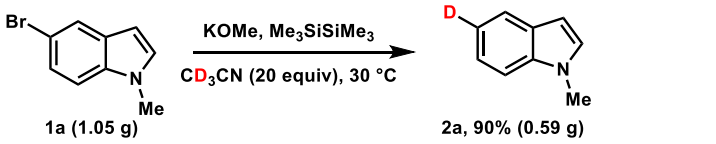
## One-Pot Halogenation and Deuteration Reaction




The bromination was conducted following procedure reported by Jiao et al.[5] To a flask equipped with a magnetic stirring bar were added methyltocopherol (83.4 mg, 0.2 mmol),

DMSO (0.22 mmol, 16 μL), hydrobromic acid (40%, 1.1 mmol) and EtOAc (1 mL). After stirring at 60 ℃ under air for 3 h, the mixture was diluted with water (15 mL) and extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine and dried over anhydrous $Na_2SO_4$. The solvents were removed under reduced pressure. The trace amount water in the crude product was removed by azeotropic distillation in anhydrous toluene (3 mL x 3) using rotovap. To the flask containing above crude product were added KOMe (28.0 mg, 0.4 mmol), $Me_3SiSiMe_3$ (80 $\mu$L, 0.4 mmol) and 1.0 mL $CD_3CN$ under argon. The mixture was stirred at 25 °C for 3 h, then diluted with water (10 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine and dried over anhydrous $Na_2SO_4$. The solvents were removed under reduced pressure and the desired product **7n** (61.4 mg, 72%) was obtained as a yellow oil after purification by silica gel chromatography (petroleum ether). $R_f$ = 0.3 (petroleum ether). $^1$H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 1H), 6.46 (s, 0.12H), 3.74 (s, 3H), 2.85 – 2.58 (m, 2H), 2.16 (s, 3H), 1.85 – 1.67 (m, 2H), 1.64 – 1.02(m, 24H), 0.96 – 0.72 (m, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.2, 146.2, 127.3, 121.0, 114.9, 75.7, 55.7, 40.1, 39.5, 37.59, 37.56, 37.4, 32.9, 32.8, 31.5, 28.1, 25.0, 24.6, 24.3, 22.9, 22.8, 21.1, 19.9, 19.8, 16.4. GCMS (EI+): calc'd for $C_{28}H_{47}DO_2$ $[M]^+$: 417.37; found: 417.4.

**Scale-up Reaction**

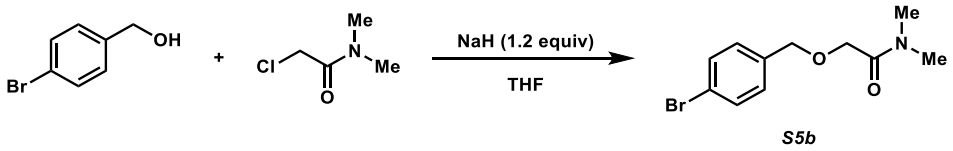



To a Schlenk tube equipped with a magnetic stirring bar, **1a** (1.05g, 5.0 mmol), KOMe (701.5 mg, 10 mmol), $Me_3SiSiMe_3$(2.0 mL, 10 mmol), and $CD_3CN$ (20 equiv, 5.2 mL) were added. The mixture was stirred at 30 ℃ for 12 h and diluted with water (30 mL). The aqueous phase was extracted with $Et_2O$ (30 mL × 3). The combined organic layers were washed with brine and dried over anhydrous $Na_2SO_4$. The solvents were removed under reduced pressure and the crude mixture was purified by silica gel chromatography (2% ethyl acetate in petroleum ether)

to provide **2a** (590.0 mg, 90% yield) as a yellow oil after purification by silica gel chromatography.

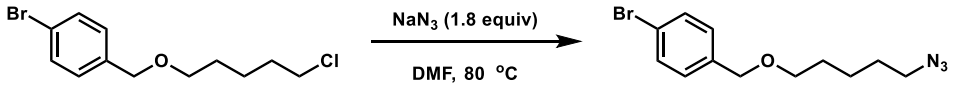
**Procedures and Spectroscopic Data for Synthese of Arylhalides**

The synthesis of **S7a**[6], **S7b**[7], **S7c**[8], **S7f**[6], **S7**[9], **S7i**[10], **S7l**[11], and **S7n**[12] were synthesized following the reported procedures.




*S5b*

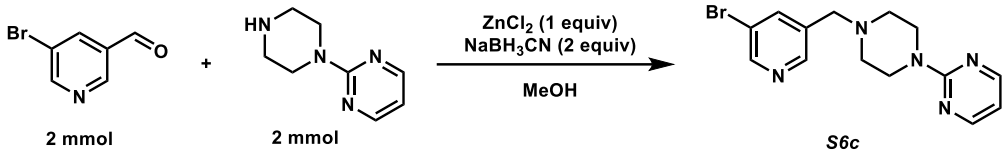
**2-((4-Bromobenzyl)oxy)-*N*,*N*-dimethylacetamide (S5b):** A Schlenk tube was charged with NaH (240.0 mg, 6 mmol) and 5 mL THF and cooled to 0 ℃. A solution of 4-bromobenzyl alcohol (935.2 mg, 5 mmol) in THF (5 mL) was added by syringe in 10 min. After the mixture was stirred at 0 ℃ for 0.5 h, a solution of 2-chloro-*N*,*N*-dimethylacetamide (607.9 mg, 5 mmol) in THF (5 mL) was added to the mixture slowly. The reaction mixture was stirred at room temperature for another 4 h, diluted with $H_2O$ (20 mL) and extracted with ethyl acetate (3 ×20 mL). The combined organic layers were washed with brine and dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The desired product **S5b** (1.17 g, 86% yield) was obtained after purification by silica gel chromatography (50% ethyl acetate in petroleum ether) as a white solid. $R_f$ = 0.3 (50% ethyl acetate in petroleum ether). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.28 – 7.23 (m, 2H), 4.57 (s, 2H), 4.17 (s, 2H), 2.97 (s, 3H), 2.96 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.0, 136.6, 131.7, 129.7, 121.9, 72.5, 69.1, 36.4, 35.6. HRMS (ESI+) calc'd for $C_{11}H_{14}BrNNaO_2$ $[M+Na]^+$: 294.0100; found 294.0101.



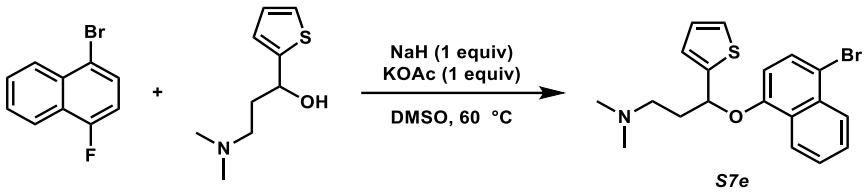

*S5c* *S5d*

**1-(((5-Azidopentyl)oxy)methyl)-4-bromobenzene (S5d)**: To a Schlenk tube equipped with a magnetic stirring bar was added a solution of **S5c** (580.0 mg, 2 mmol) in DMF (5mL), followed by sodium azide (234.0 mg, 3.6 mmol). The reaction mixture was stirred at 80 ℃ for 3 h. After cooled to room temperature, the mixture was diluted with $H_2O$ (20 mL) and extracted with ethyl acetate (3 ×20 mL). The combined organic layers were washed with brine and dried over

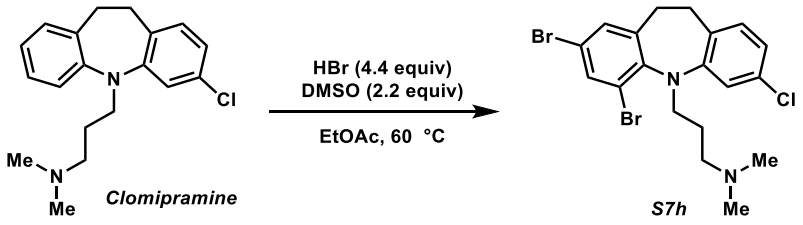
anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The desired product **S5d** (346.4 mg, 58% yield) was obtained after purification by silica gel chromatography (2% ethyl acetate in petroleum ether) as a yellowoil. $R_f$ = 0.3 (2% ethyl acetate in petroleum ether). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 4.44 (s, 2H), 3.46 (t, *J* = 6.4 Hz, 2H), 3.27 (t, *J* = 6.9 Hz, 2H), 1.63 (m, 4H), 1.52 – 1.41 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.6, 131.5, 129.3, 121.4, 72.2, 70.2, 51.4, 29.3, 28.7, 23.5. HRMS (ESI+) calc'd for $C_{12}H_{16}BrN_3NaO$ $[M+Na]^+$: 320.0369; found 320.0378.



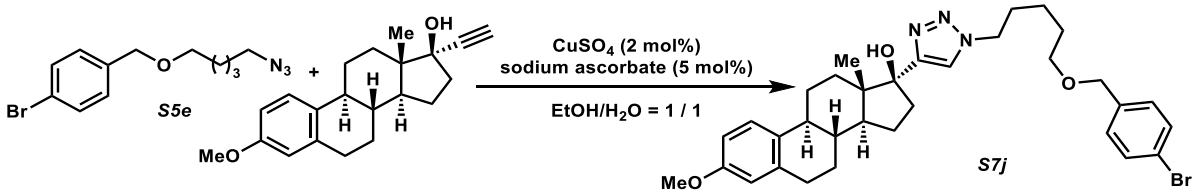

**2-(4-((5-bromopyridin-3-yl)methyl)piperazin-1-yl)pyrimidine (S6c):** To a round-bottomed flask equipped with a magnetic stirring bar, 5-bromonicotinaldehyde (372.0 mg, 2 mmol), 2-(piperazin-1-yl)pyrimidine (328.4 mg, 2 mmol), $ZnCl_2$ (136.3 mg, 1 mmol) and MeOH (5 mL) were added sequentially. After the reaction mixture was stirred at room temperature for 1 h, $NaBH_3CN$ (125.6 mg, 2 mmol) was added and stirred for another 3 h. Solvent was removed under reduced pressure and the residue was partitioned between 1 N NaOH and $CH_2Cl_2$. The phases were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layers were washed with brine and dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The desired product **S6c** (427.5 mg, 64% yield) was obtained after purification by silica gel chromatography (33% ethyl acetate in petroleum ether) as a white solid. $R_f$ = 0.3 (33% ethyl acetate in petroleum ether). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 2.0 Hz, 1H), 8.48 (d, *J* = 1.4 Hz, 1H), 8.30 (d, *J* = 4.7 Hz, 2H), 7.96 (s, 1H), 6.50 (t, *J* = 4.7 Hz, 1H), 3.88 (s, 4H), 3.59 (s, 2H), 2.57 (s, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 161.6, 157.9, 150.3, 148.6, 139.6, 121.1, 110.3, 100.1, 59.5, 53.0, 43.4. HRMS (ESI+) calc'd for $C_{14}H_{17}BrN_5$ $[M+H]^+$: 334.0662; found 334.0665.




**3-((4-Bromonaphthalen-1-yl)oxy)-*N*,*N*-dimethyl-3-(thiophen-2-yl)propan-1-amine (S7e):** The reported procedure was followed.[13] To a Schlenk tube equipped with a magnetic stirring bar, NaH (80.0 mg, 2 mmol) was added to the solution of 3-(dimethylamino)-1-(thiophen-2-yl)propan-1-ol (520.0 mg, 2 mmol) in DMSO (3 mL). The reaction mixture was stirred at room temperature for 20 min. Then KOAc (196.3 mg, 2 mmol) was added. After the mixture was stirred for another 15 min, 1-bromo-4-fluoronaphthalene (540.1 mg, 2.4 mmol) was added. The mixture was stirred at 60 ℃ overnight. Then the reaction mixture was diluted with water (10 mL), and the pH was adjusted to 5 – 6 by the addition of acetic acid carefully. The mixture was then extracted with hexane to remove unreacted aryl fluoride substrate. The pH of aqueous phase was adjusted to 10 – 12 by the addition of sodium hydroxide solution, and then extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The desired product **S7e** (662.8 mg, 85% yield) was obtained after purification by silica gel chromatography (2% methanol in dichloromethane) as an amber oil. $R_f$ = 0.4 (2% methanol in dichloromethane). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 7.64 – 7.57 (m, 1H), 7.57 – 7.50 (m, 2H), 7.22 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.05 (d, *J* = 3.1 Hz, 1H), 6.94 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 5.75 (t, *J* = 6.2 Hz, 1H), 2.53 – 2.46 (m, 2H), 2.46 – 2.38 (m, 1H), 2.25 (s, 6H), 2.23 – 2.14 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.2, 144.7, 132.6, 129.4, 127.7, 127.4, 126.9, 126.6, 126.0, 124.94, 124.89, 122.6, 113.6, 107.8, 74.9, 55.7, 45.6, 36.9. HRMS (ESI+) calc'd for $C_{19}H_{21}BrNOS$ $[M+H]^+$: 392.0502; found 392.0504.

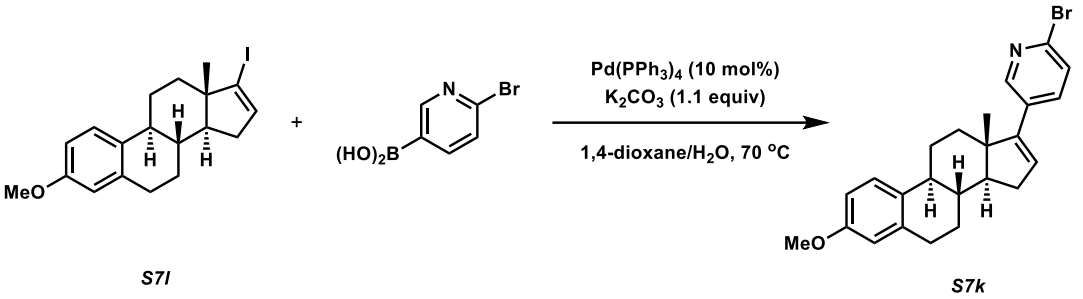


**3-(2,4-dibromo-7-chloro-10,11-dihydro-5H-dibenzo[*b,f*]azepin-5-yl)-N,N-dimethylpropan-1-amine (S7h):** The reported procedure was followed.[5] Clomipramine (157.4 mg, 0.5 mmol) and DMSO (78 μL, 1.1 mmol) were dissolved in EtOAc (2 mL) in a flask. Aqueous hydrobromic acid (40%, 444 mg, 2.2 mmol) was added to the flask at 60 ℃ and the mixture was stirred for 5 h. After cooling down to room temperature, the reaction was diluted with EtOAc (5 mL) and the pH was adjusted to 8 – 9 by addition of 20% NaOH aqueous solution. The organic layers were washed with water (3 × 5 mL), brine and dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (5% methanol in dichloromethane) to afford the brominated product **S7h** (195.1 mg, 83%) of as a yellow oil. $R_f$ = 0.3 (5% methanol in dichloromethane. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.25 – 7.21 (m, 2H), 7.11 (s, 1H), 6.92 (d, *J* = 9.2 Hz, 1H), 3.66 (t, *J* = 6.9 Hz, 2H), 3.10 – 2.99 (m, 4H), 2.29 (t, *J* = 7.1 Hz, 2H), 2.17 (s, 6H), 1.76 – 1.62 (m, 2H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.8, 146.6, 137.2, 134.6, 133.2, 132.2, 131.7, 129.7, 122.5, 121.6, 116.4, 114.7, 57.3, 49.1, 45.5, 31.7, 31.1, 25.8. HRMS (ESI+) calc'd for $C_{19}H_{22}Br_2ClN_2$ $[M+H]^+$: 470.9833; found 470.9841.




***(8R,9S,13S,14S,17S)*-17-(1-(5-((4-bromobenzyl)oxy)pentyl)-1*H*-1,2,3-triazol-4-yl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol (S7j)**: The reported procedure was followed.[14] To a screw-capped vial equipped with a magnetic stirring bar, **S5e** (148.5 mg, 0.5 mmol), alkyne (159.2 mg, 0.5 mmol), and a 1:1 mixture of ethanol and water (2 mL) were added, followed by the addition of sodium ascorbate (9.9 mg, 10 mol%) and $CuSO_4$•H2O (6.3 mg, 5 mol%). The reaction mixture was stirred at room temperature for 12 h, diluted with $H_2O$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were washed with brine and dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The desired product **S7i** (232.4 mg, 76% yield) was obtained after purification by silica gel chromatography (33% ethyl acetate in petroleum ether) as a white solid. $R_f$ = 0.2 (33% ethyl

acetate in petroleum ether). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.40 (s, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 1H), 6.67 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.61 (d, *J* = 2.5 Hz, 1H), 4.46 – 4.27 (m, 4H), 3.76 (s, 3H), 3.44 (t, *J* = 6.3 Hz, 2H), 2.87 – 2.82 (m, 2H), 2.46 – 2.30 (m, 1H), 2.15 – 2.12 (m, 3H), 1.98 – 1.91z (m, 5H), 1.68 – 1.58 (m, 4H), 1.59 – 1.26 (m, 5H), 1.04 (s, 3H), 0.65 (td, *J* = 12.8, 3.8 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.1, 157.5, 153.6, 138.1, 137.5, 132.6, 131.6, 129.4, 126.4, 121.2, 113.9, 111.5, 82.5, 72.3, 70.1, 55.3, 50.4, 48.7, 47.5, 43.5, 39.6, 38.1, 33.1, 30.2, 30.0, 29.2, 27.5, 26.4, 23.5, 23.4, 14.4. HRMS (ESI+) calc'd for $C_{33}H_{43}BrN_3O_3$ $[M+H]^+$: 608.2482; found 608.2480.




*S7l* *S7k*

**2-bromo-5-((8S,9S,13S,14S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)pyridine** (***S7k***): To a Schlenk tube equipped with a magnetic stirring bar, **S7l** (197.1 mg, 0.5 mmol), $K_2CO_3$ (345.6 mg, 0.55 mmol), and (6-bromopyridin-3-yl) boronic acid (110.5 mg, 0.55 mmol) were added. Then l,4-dioxane (18 mL) and degassed $H_2O$ (7 mL) were added using syringe. After the mixture was stirred at room temperature for 15 min, $Pd(PPh)_4$ (57.8 mg, 0.05 mmol) was added and the reaction was heated to 70 ℃ and stirred for 18 h. Dioxane was removed under reduced pressure and the resulted solution was diluted with water (20 mL), and extracted with $CH_2Cl_2$ (30 mL x 3). The combined organic layers were washed with brine and dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The desired product **S7k** (81.4 mg, 38% yield) was obtained after purification by silica gel chromatography (2% ethyl acetate in petroleum ether) as a brown solid. $R_f$ = 0.2 (2% ethyl acetate in petroleum ether). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 2.3 Hz, 1H), 7.55 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.66 (d, *J* = 2.6 Hz, 1H), 6.05 (dd, *J* = 3.1, 1.7 Hz, 1H), 3.79 (s, 3H), 2.93 (dd, *J* = 12.5, 6.3 Hz, 2H), 2.45 – 2.25 (m, 3H), 2.21 – 2.05 (m, 2H), 2.01 – 1.90 (m, 1H), 1.81 (td, *J* = 11.4, 6.5 Hz, 1H), 1.75 – 1.59 (m, 3H), 1.48 (ddd, *J* = 24.1,

11.8, 7.0 Hz, 1H), 2.78 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.6, 150.7, 148.1, 140.1, 138.0, 136.4, 132.6, 132.4, 130.2, 127.6, 126.2, 114.0, 111.6, 56.8, 55.3, 47.8, 44.1, 37.4, 35.4, 31.7, 29.8, 27.8, 26.6, 16.8. HRMS (ESI+) calc'd for $C_{24}H_{27}BrNO$ $[M+H]^+$: 424.1271; found 424.1262.

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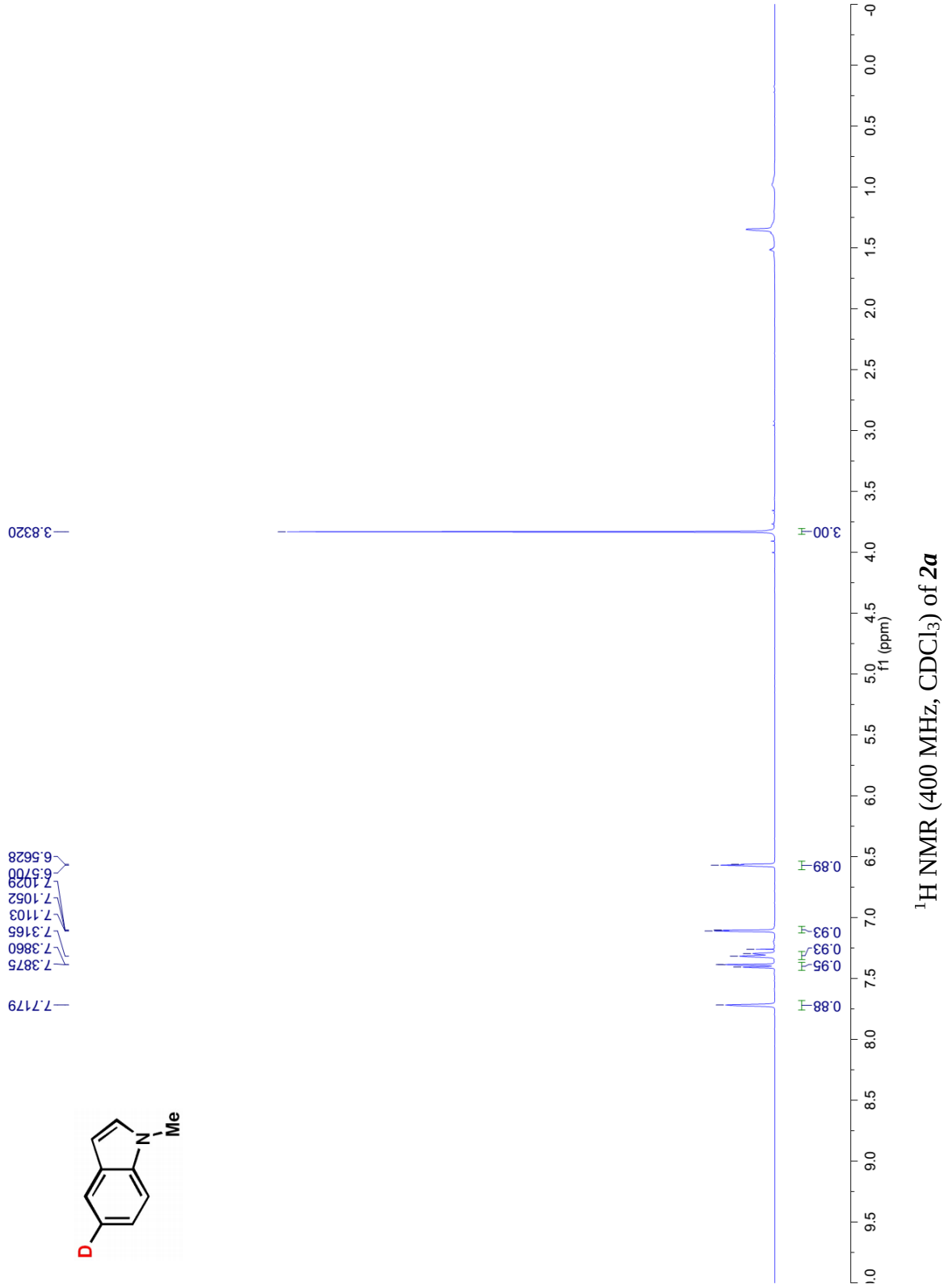
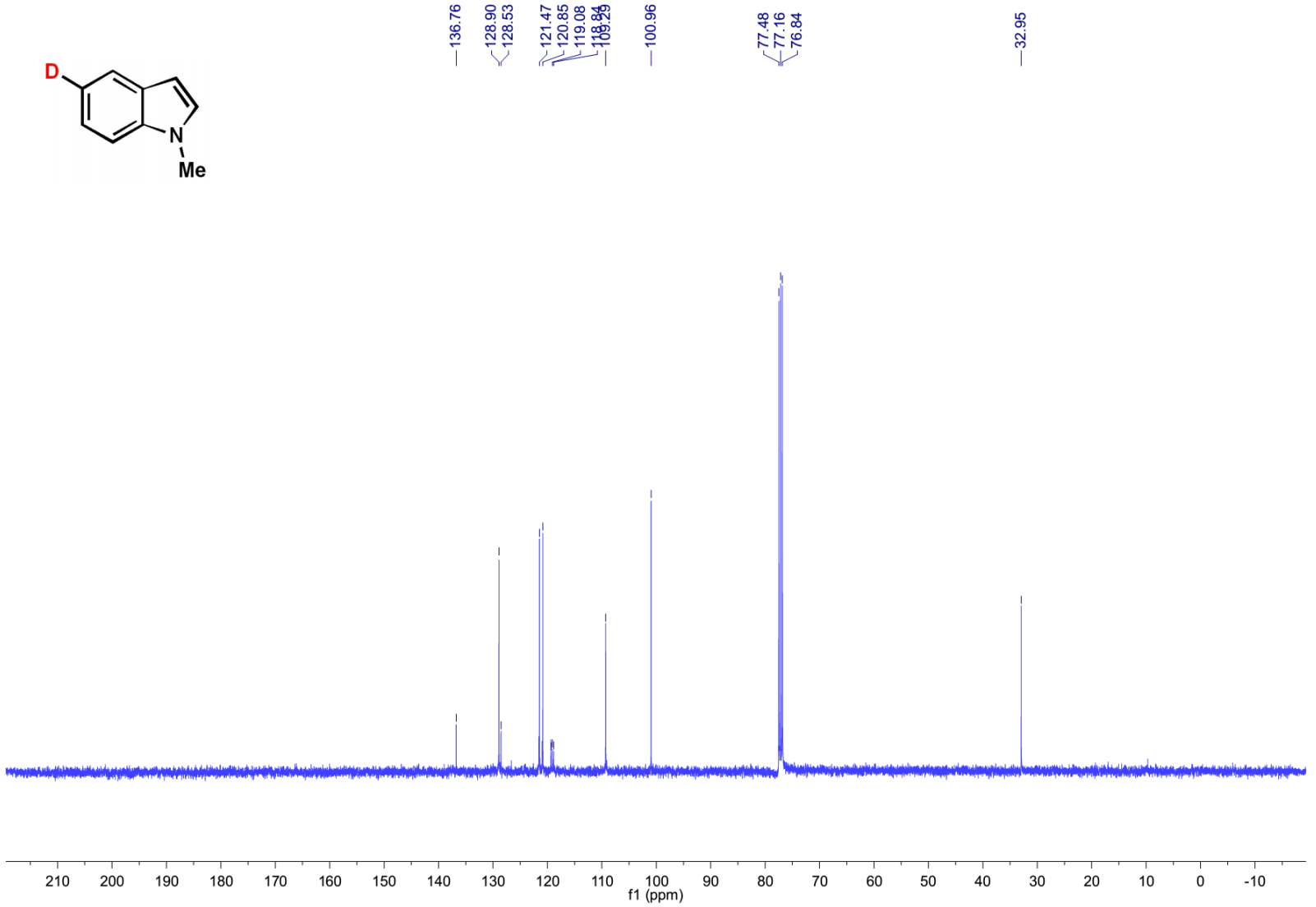
## $^{1}$H NMR and $^{13}$C NMR Spectra for Deuterated Compounds

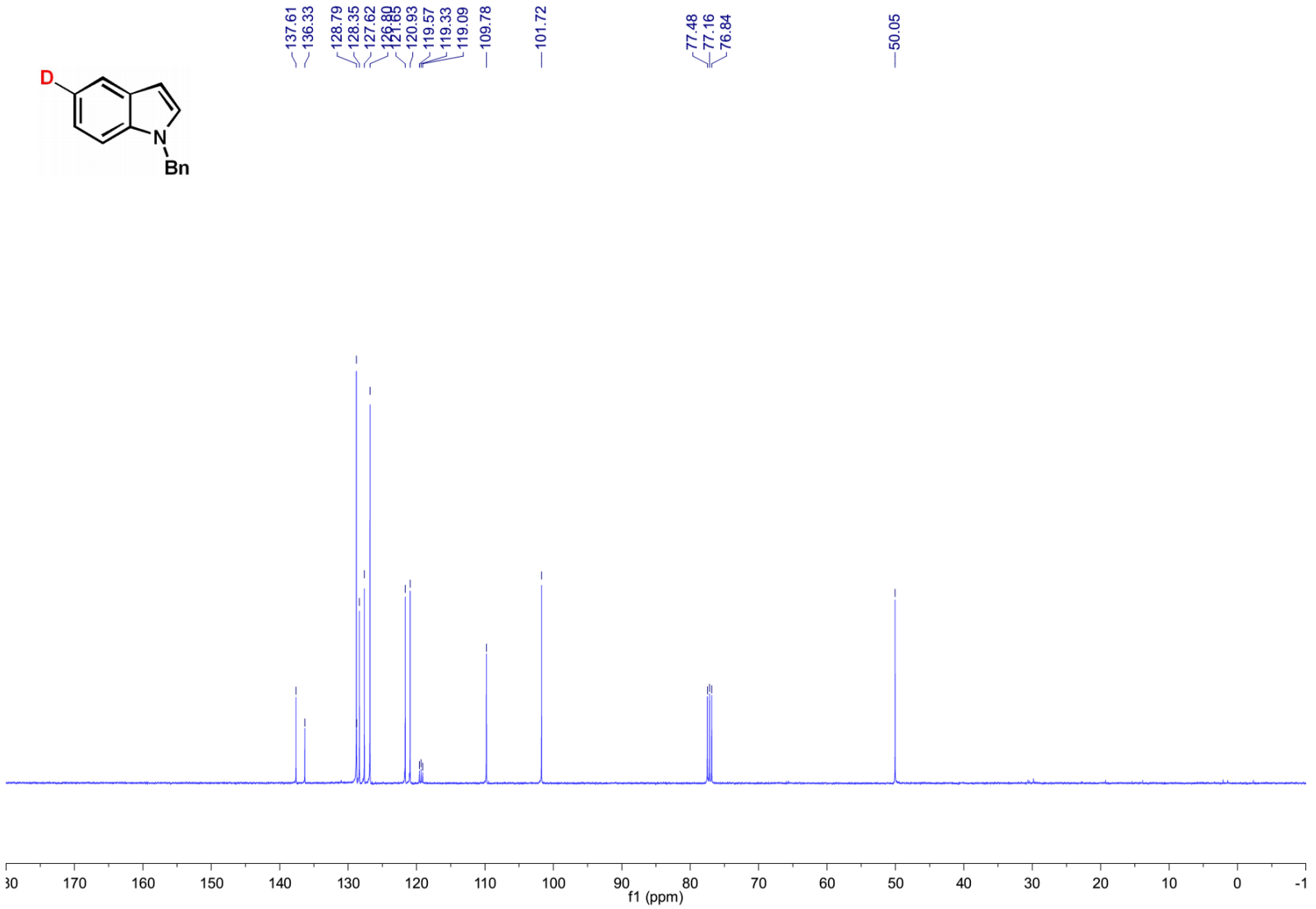



$^{1}$H NMR (400 MHz, $CDCl_3$) of ***2a***

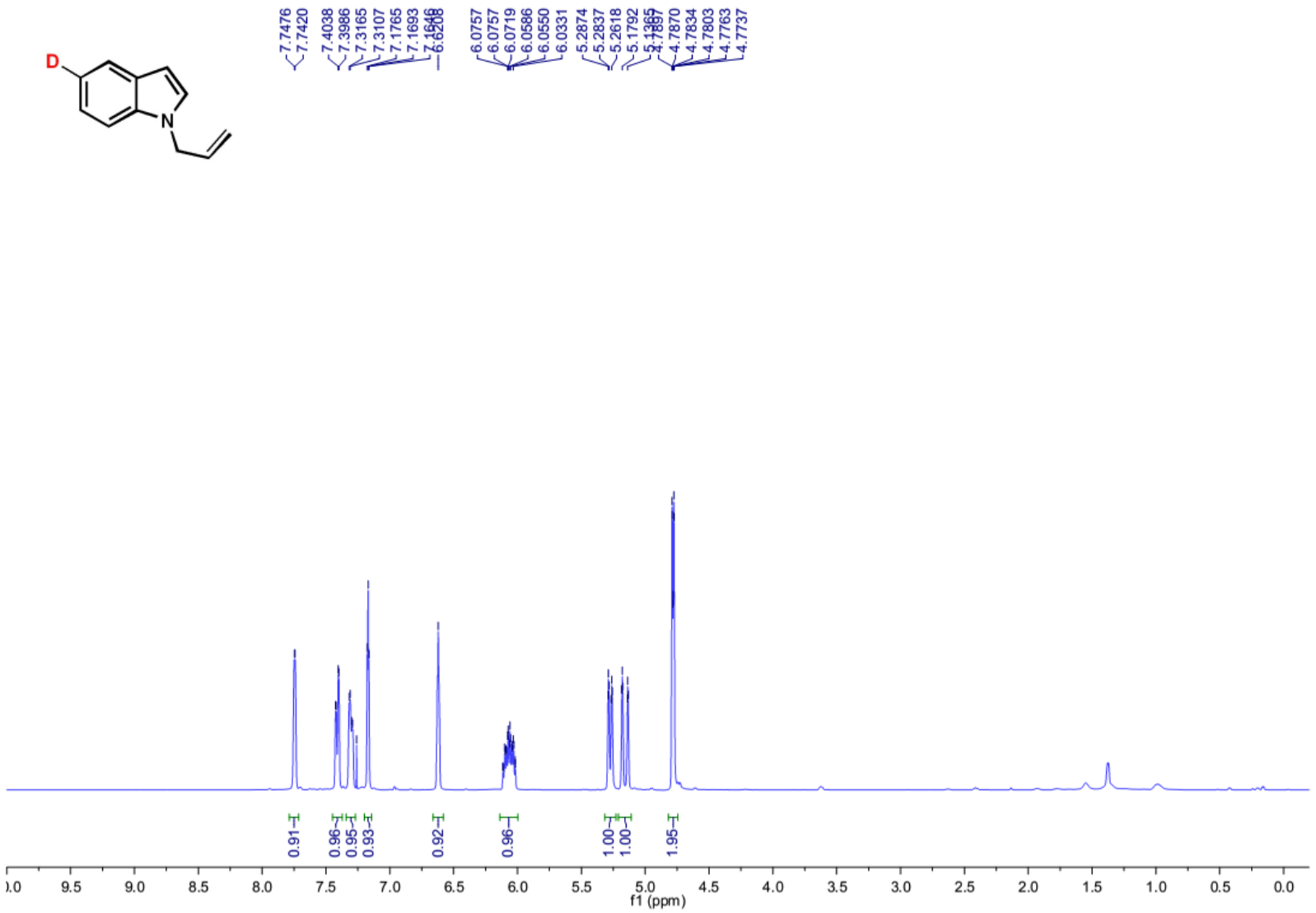



$^{13}$C NMR (100 MHz, $CDCl_3$) of ***2a***

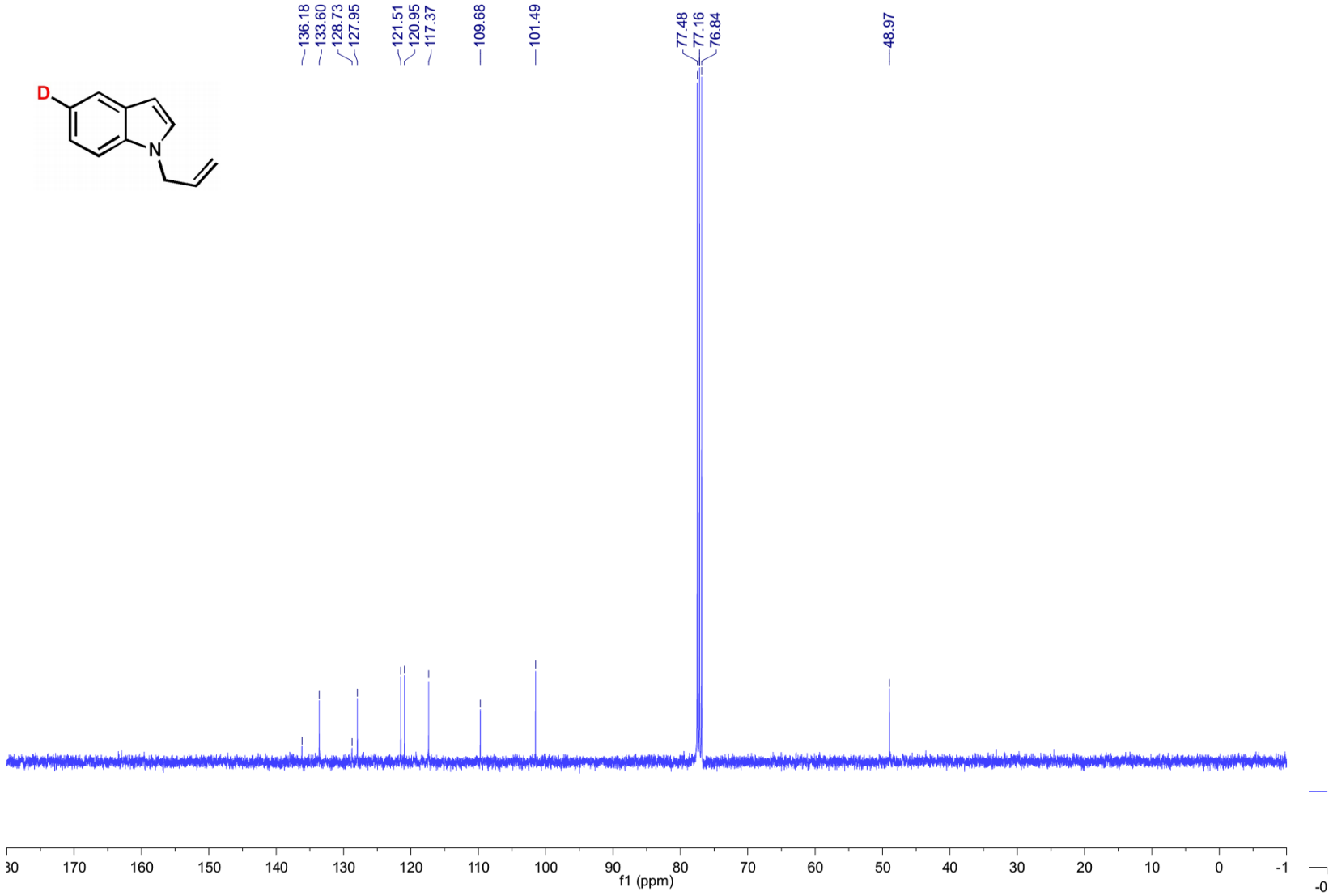

$^1$H NMR (400 MHz, $CDCl_3$) of ***2b***




$^{13}$C NMR (100 MHz, $CDCl_3$) of ***2b***




$^{1}$H NMR (400 MHz, $CDCl_3$) of ***2c***

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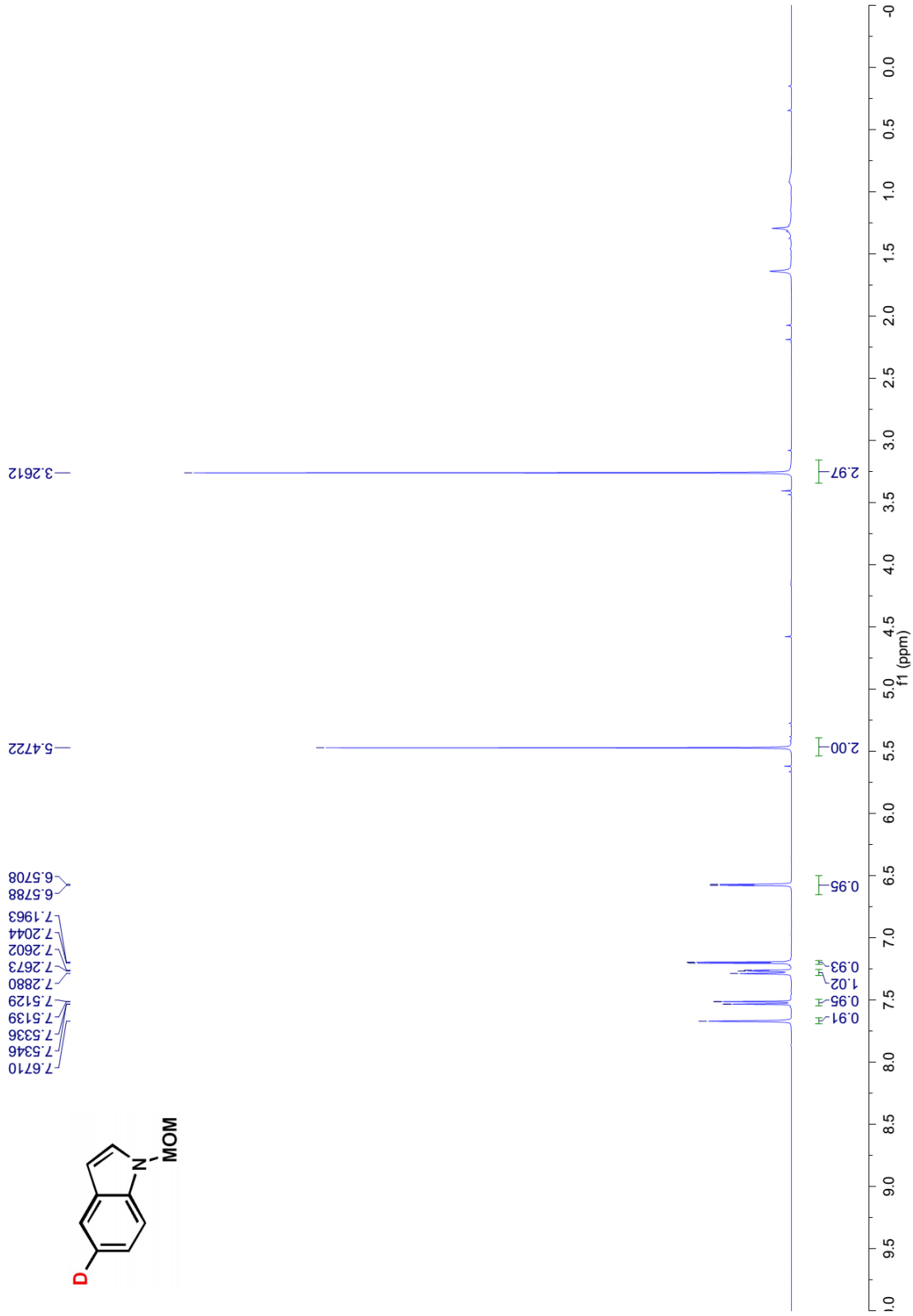
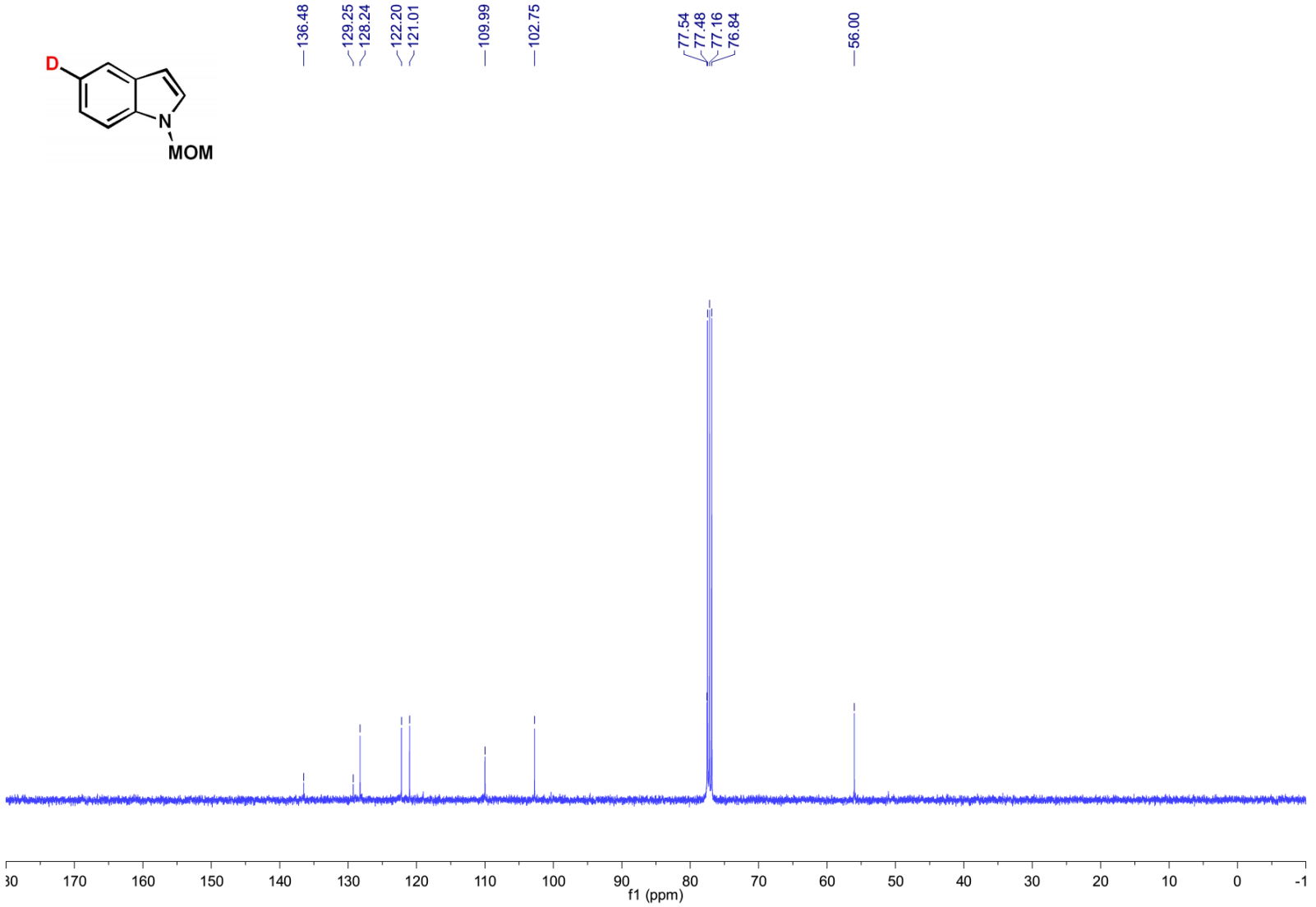
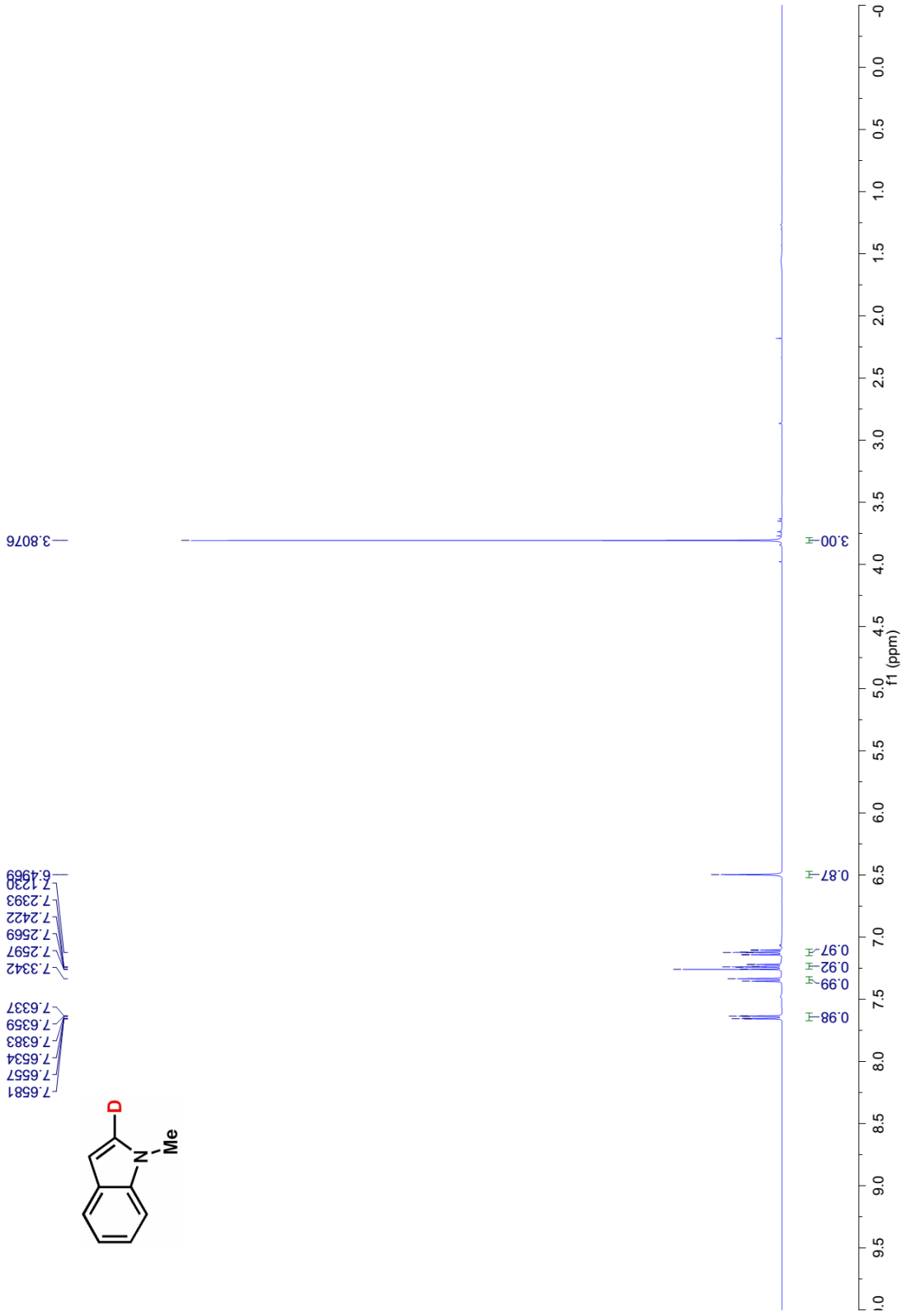


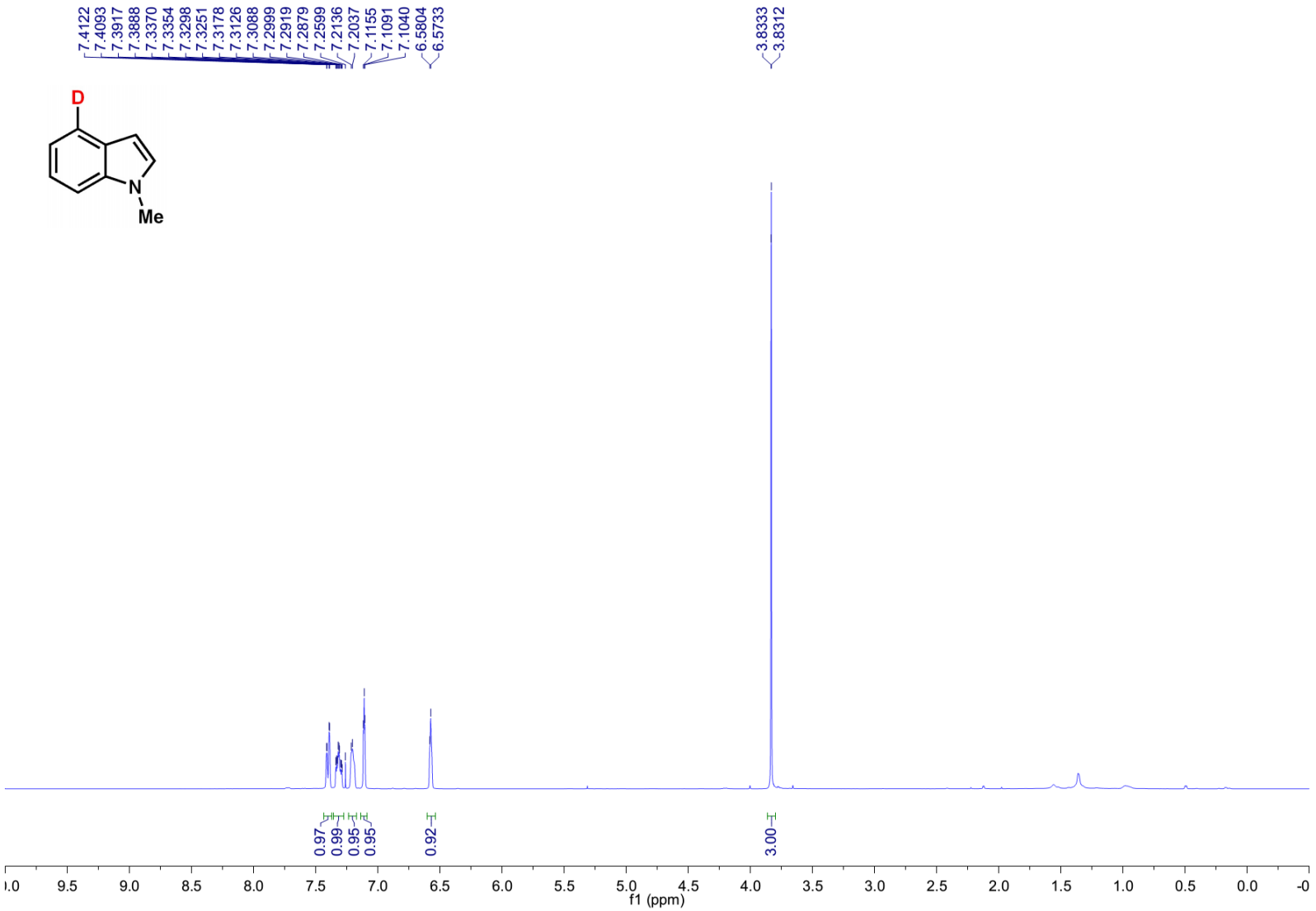

$^1$H NMR (400 MHz, $CDCl_3$) of ***2d***



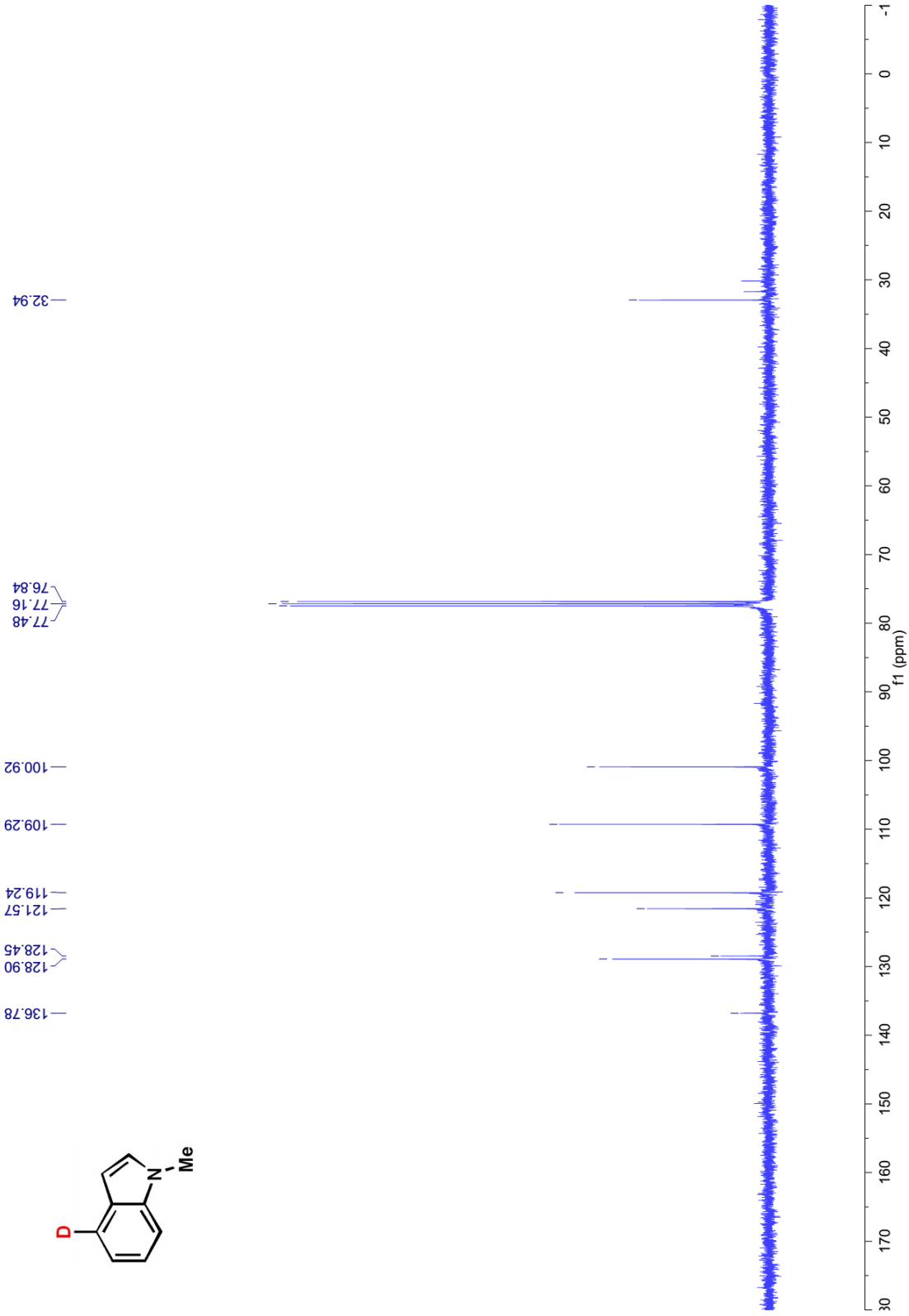

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***2d***



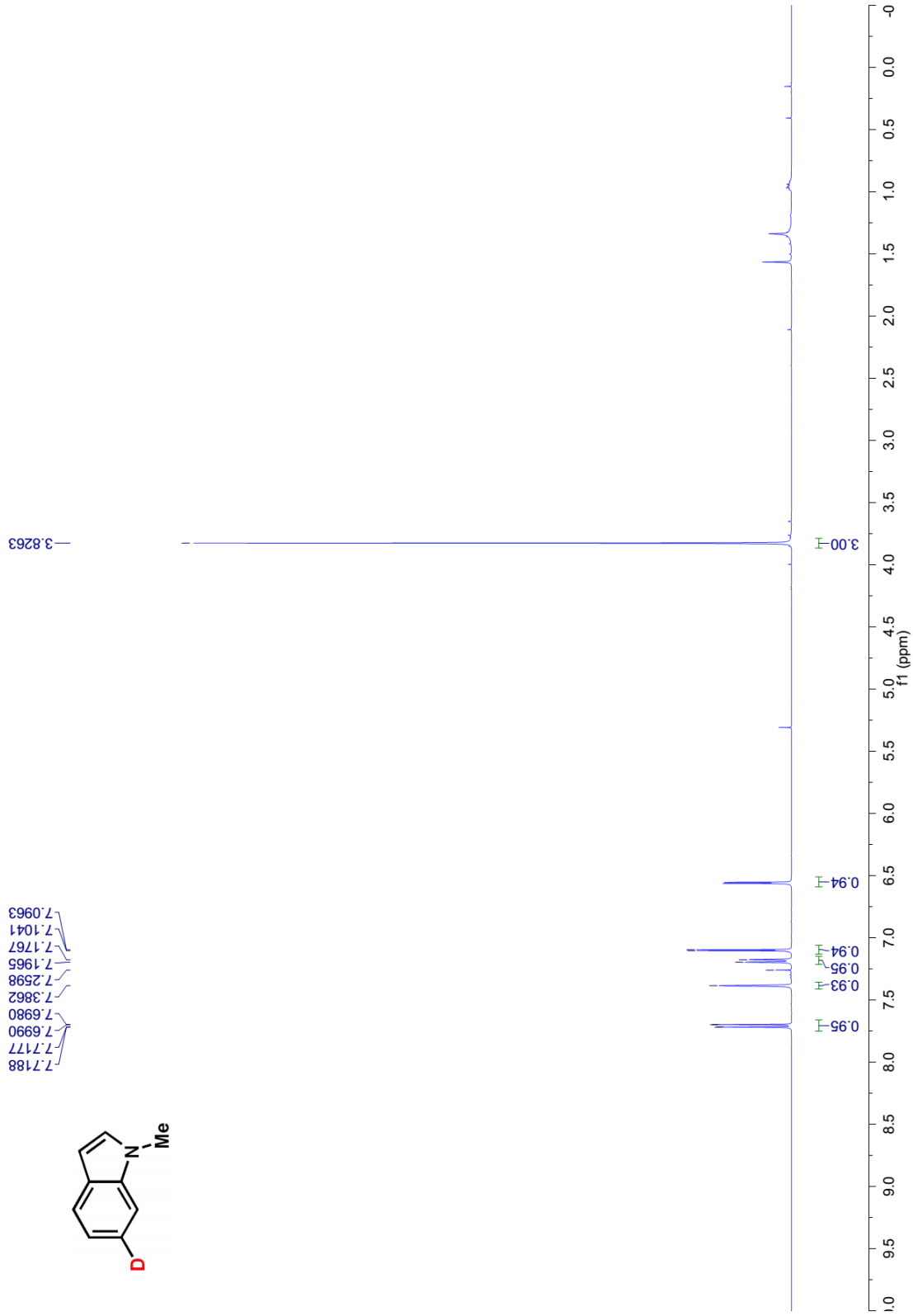

$^1$H NMR (400 MHz, $CDCl_3$) of ***2e***



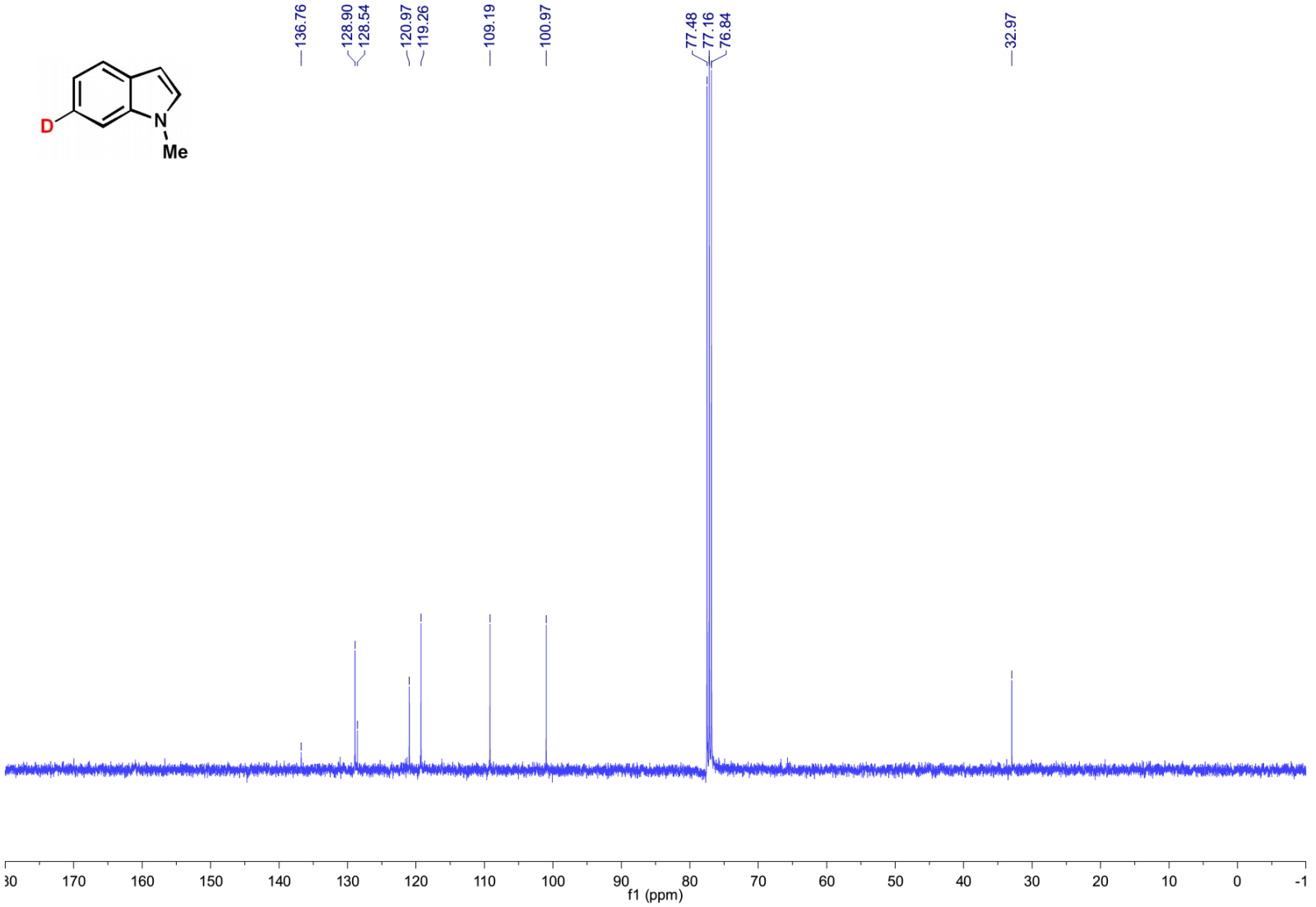

$^{1}$H NMR (400 MHz, $CDCl_3$) of ***2f***



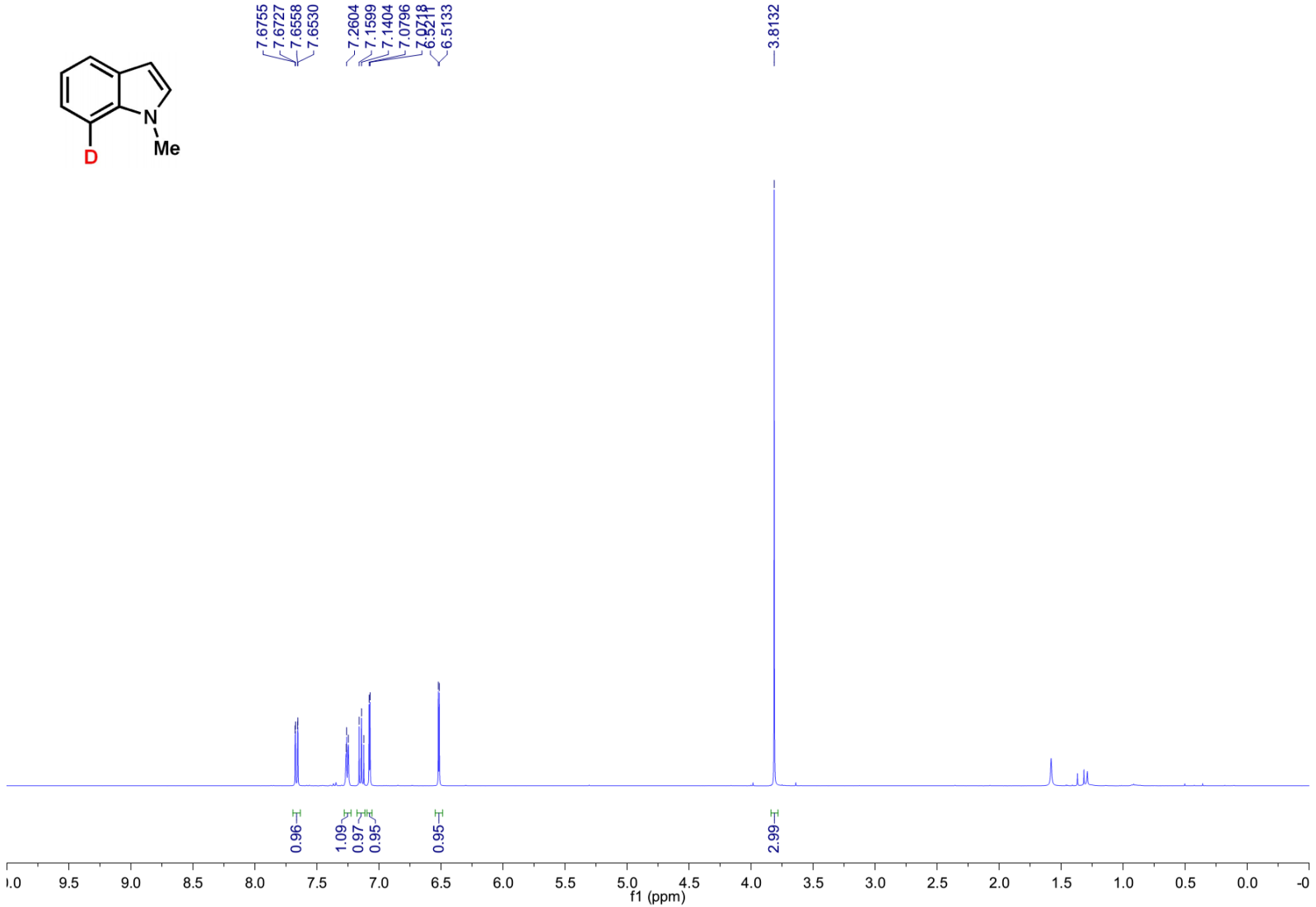

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***2f***



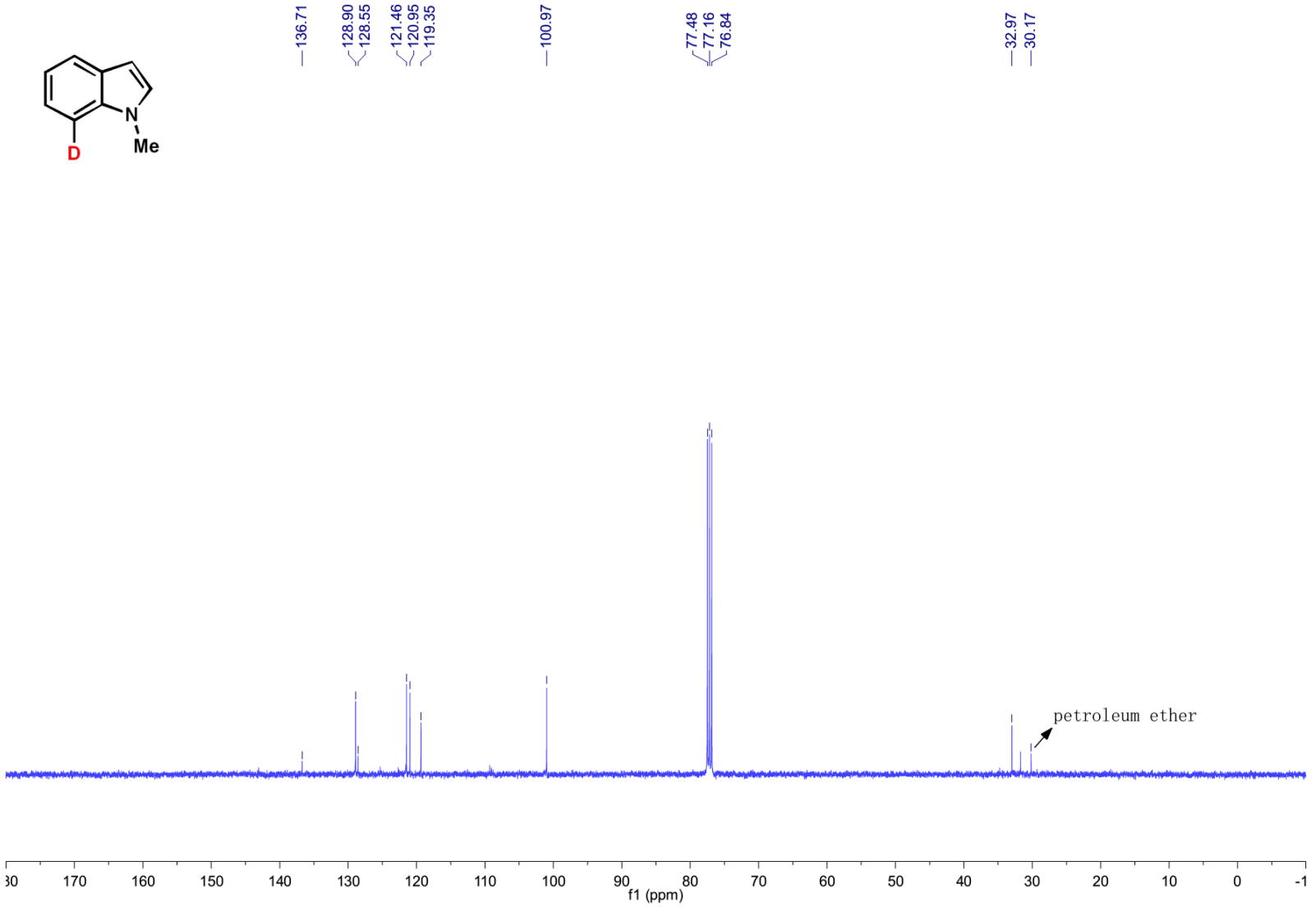

$^1$H NMR (400 MHz, $CDCl_3$) of ***2g***



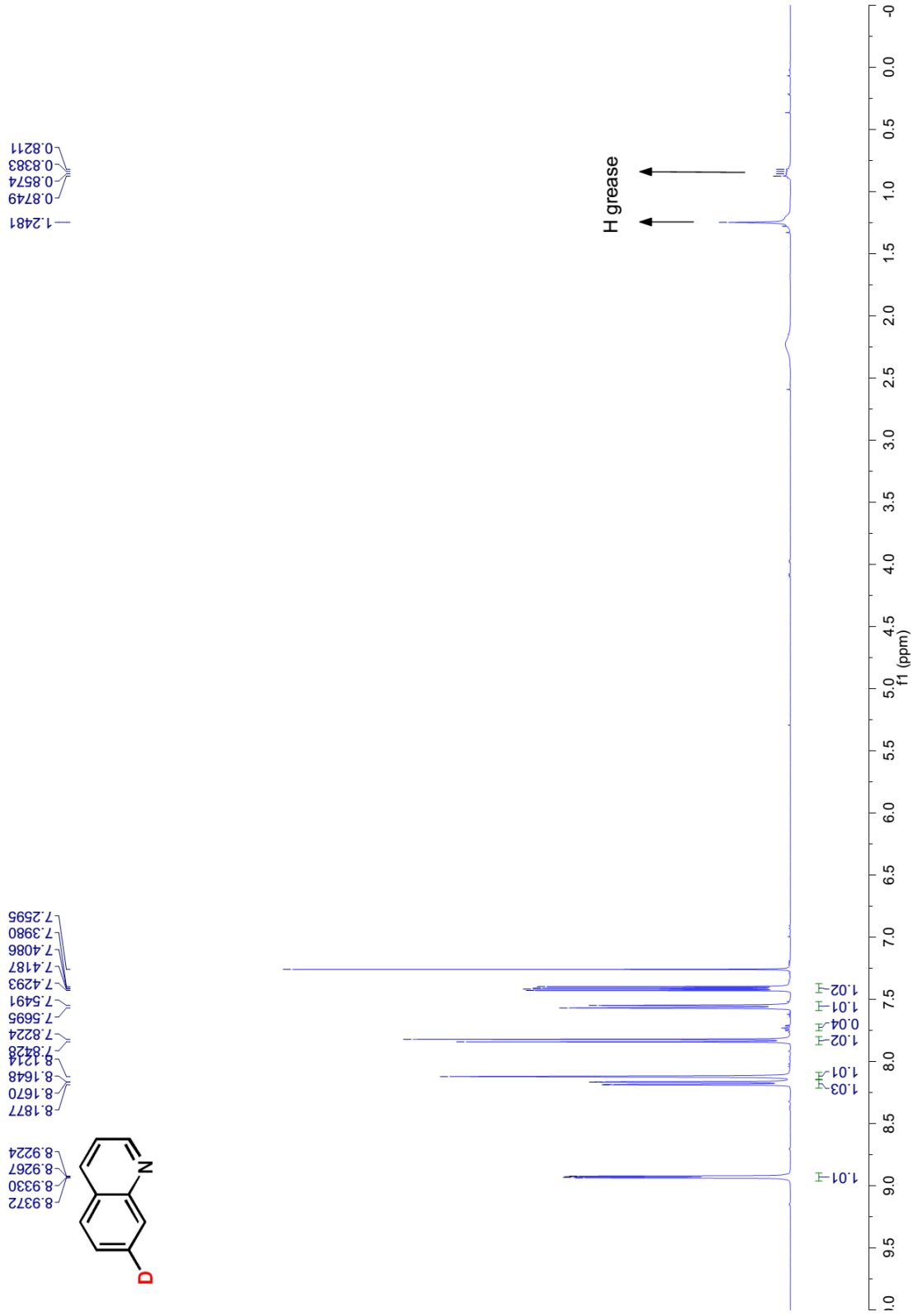

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***2g***



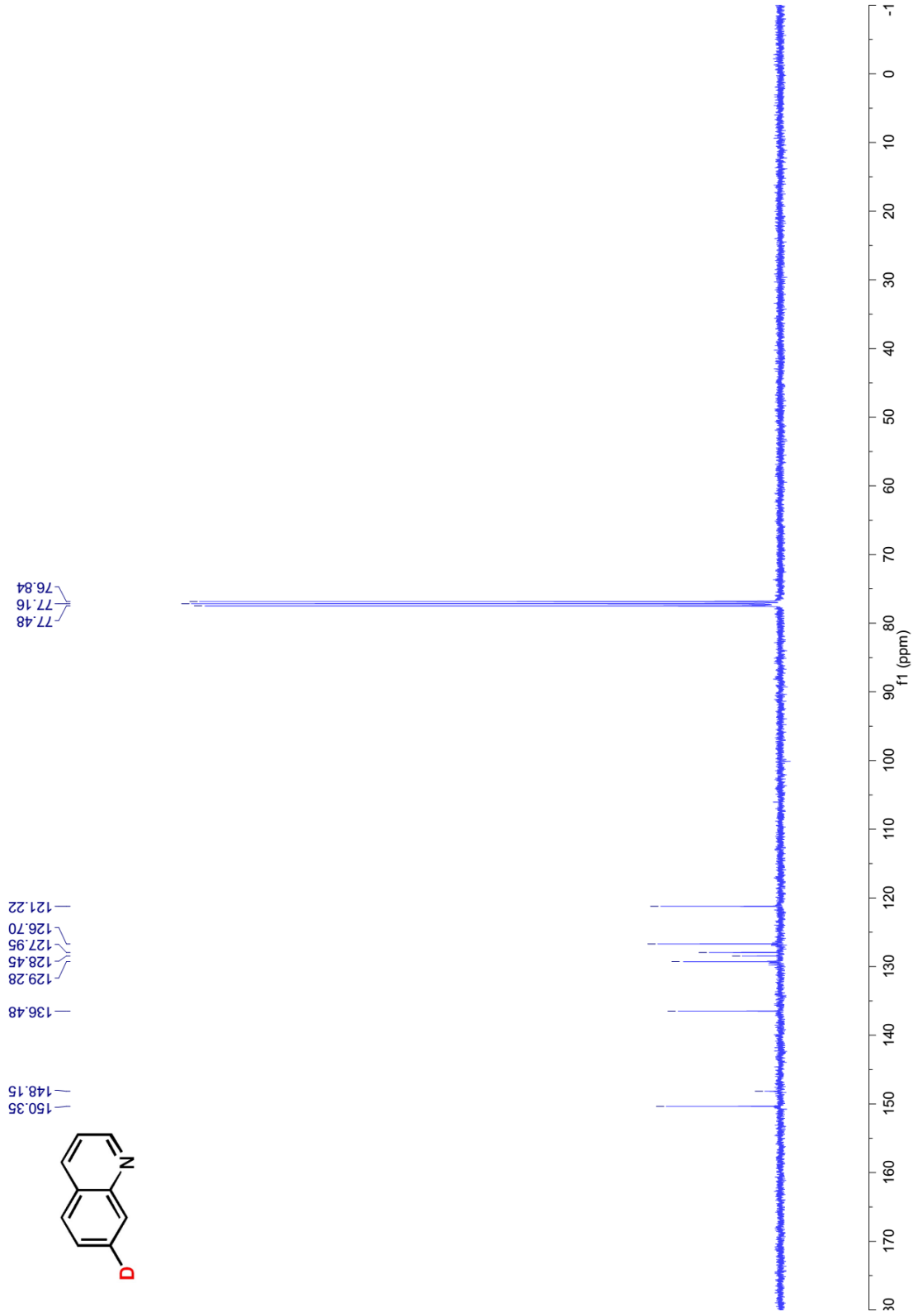

$^{1}$H NMR (400 MHz, $CDCl_3$) of ***2h***



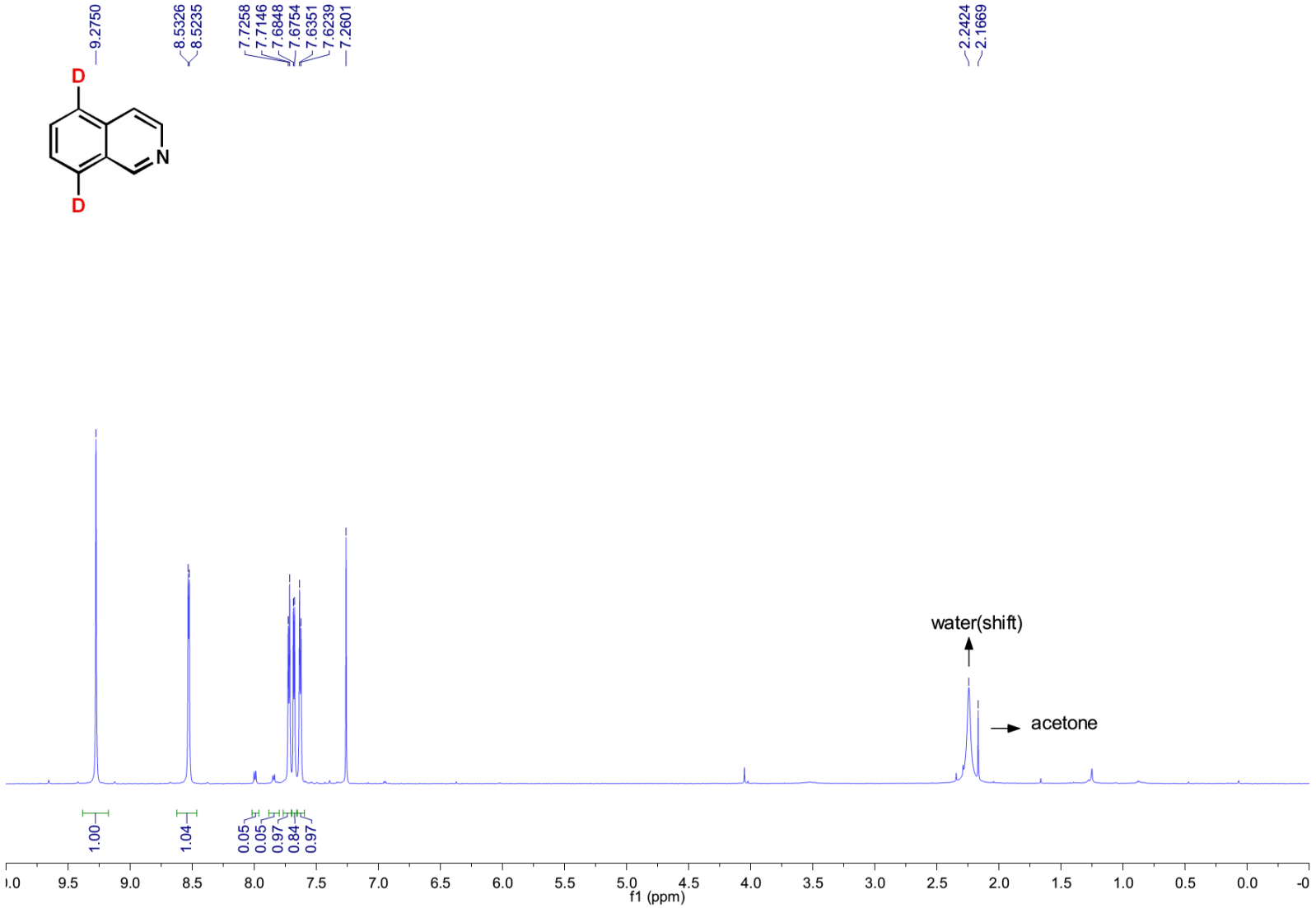

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***2h***



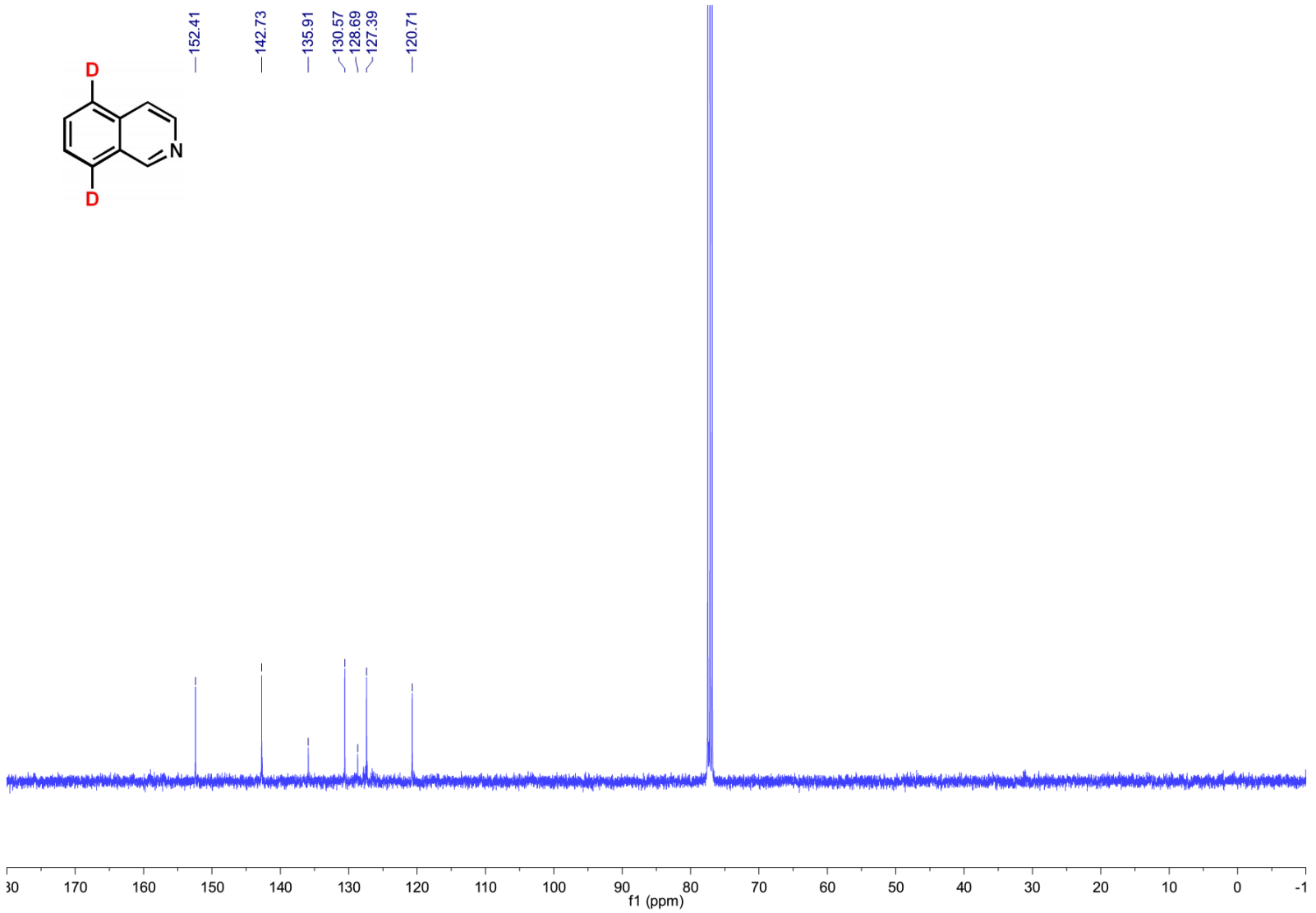

$^1$H NMR (400 MHz, $CDCl_3$) of ***3a***




$^{13}$C NMR (100 MHz, $CDCl_3$) of ***3a***




$^1$H NMR (400 MHz, $CDCl_3$) of ***3b***

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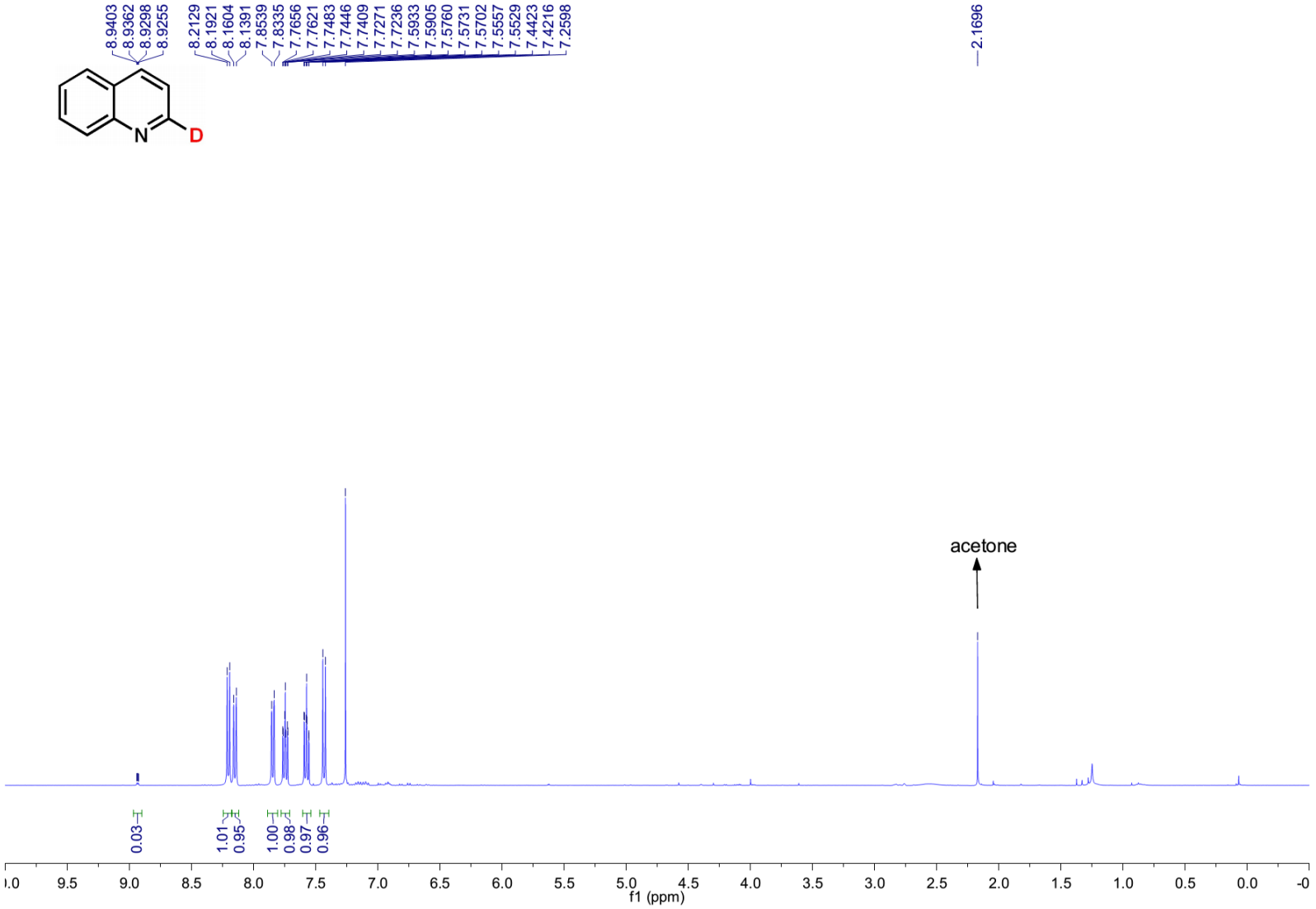
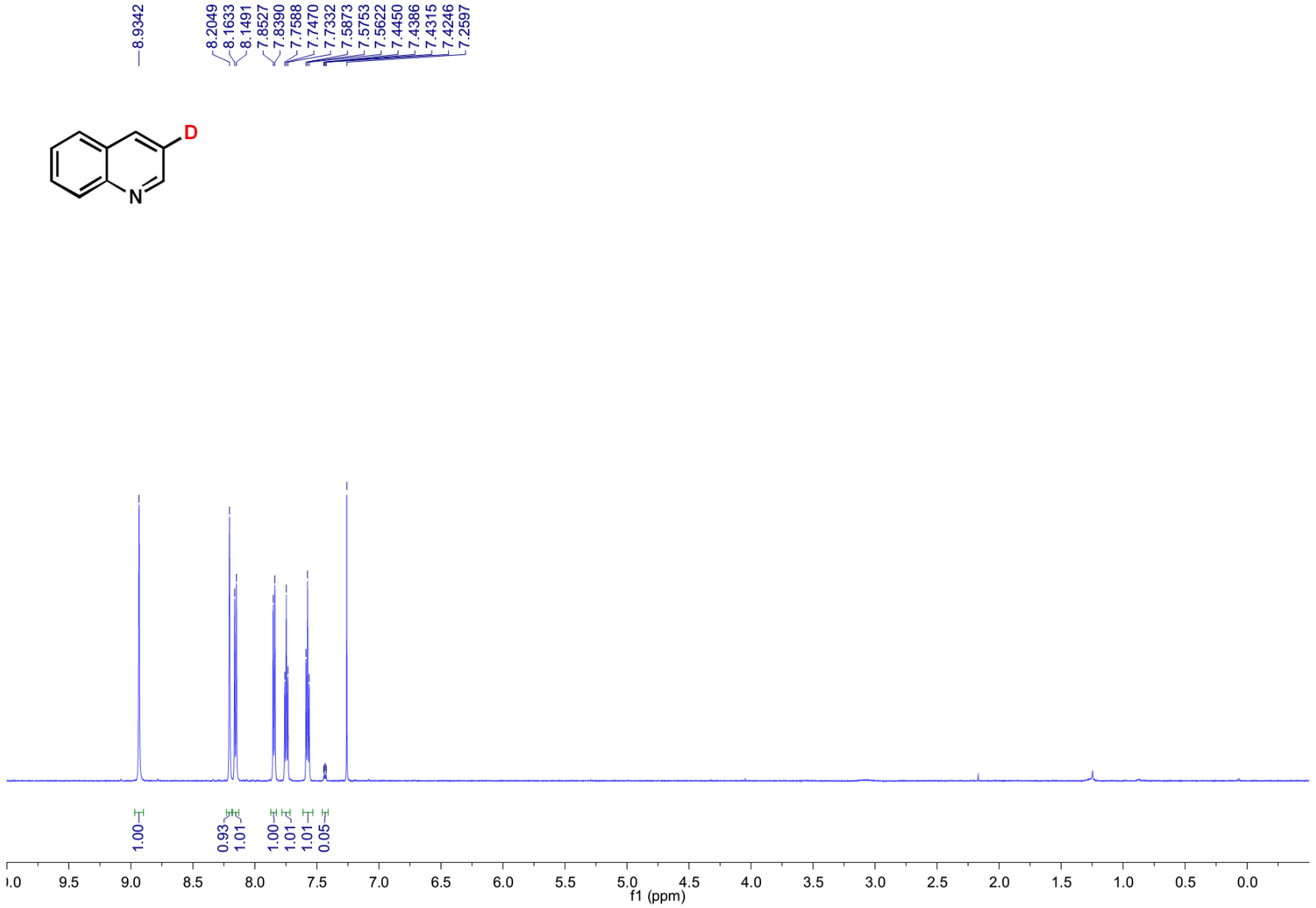
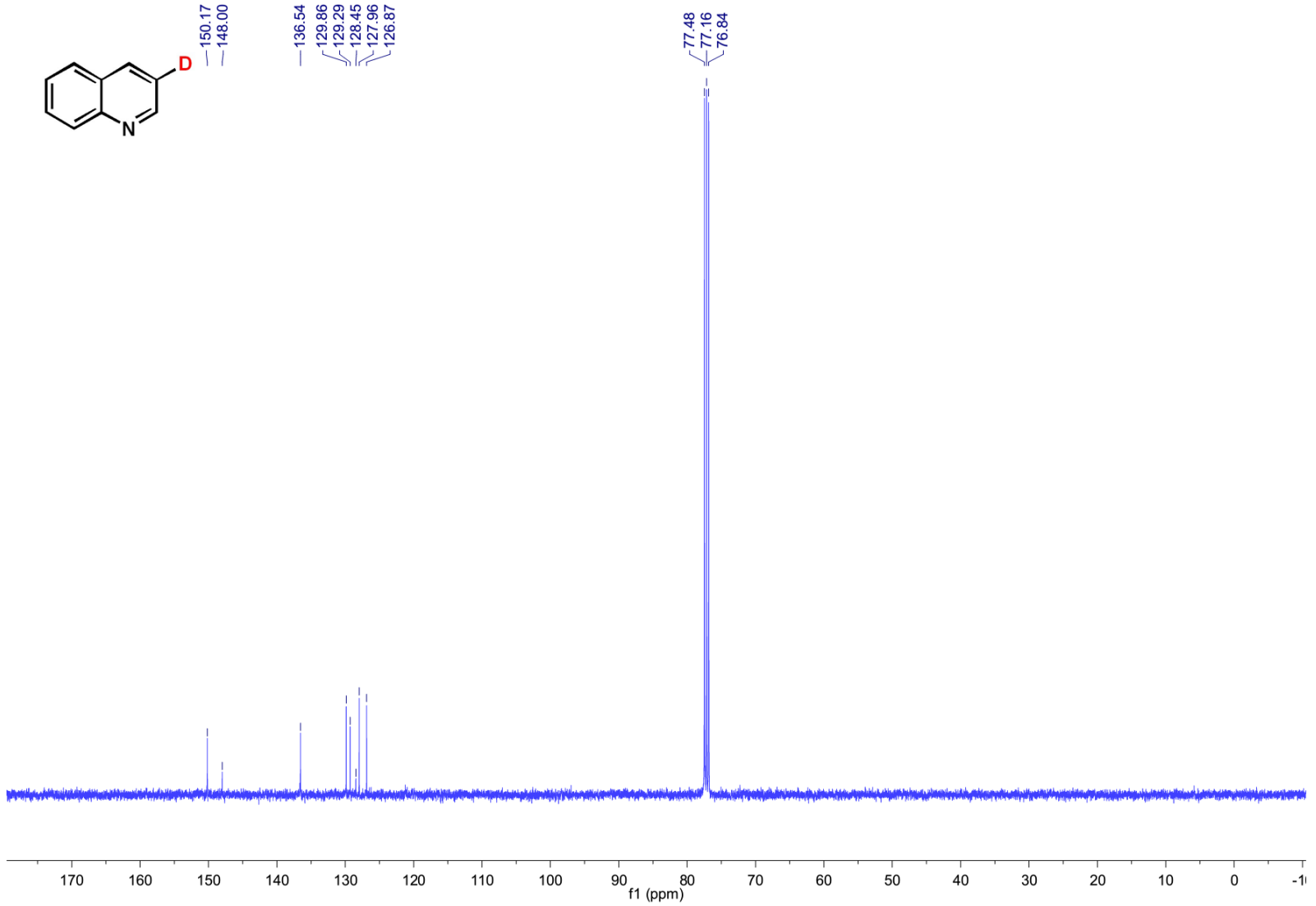



$^{1}$H NMR (400 MHz, $CDCl_3$) of ***3c***




$^1$H NMR (400 MHz, $CDCl_3$) of ***3d***

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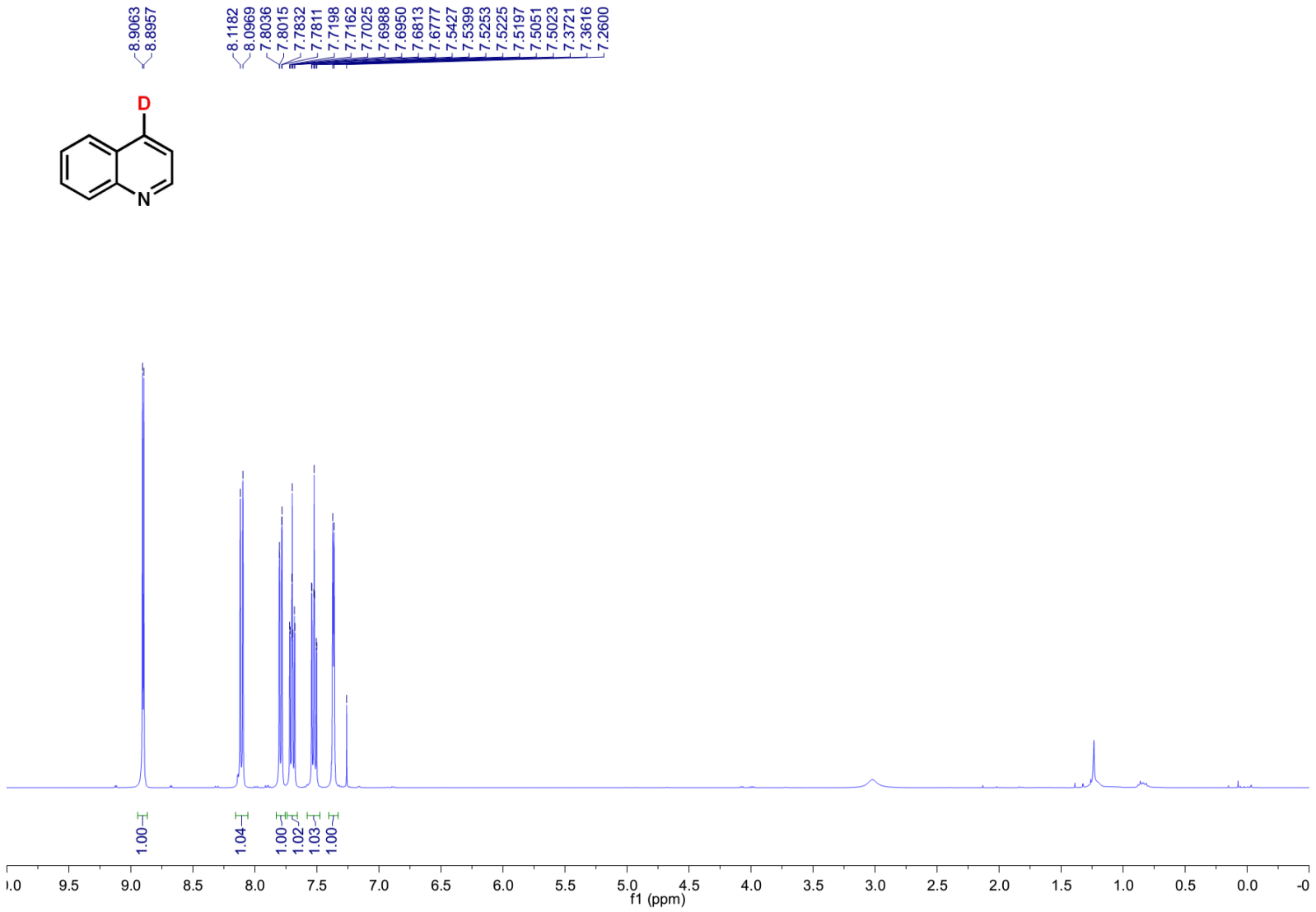


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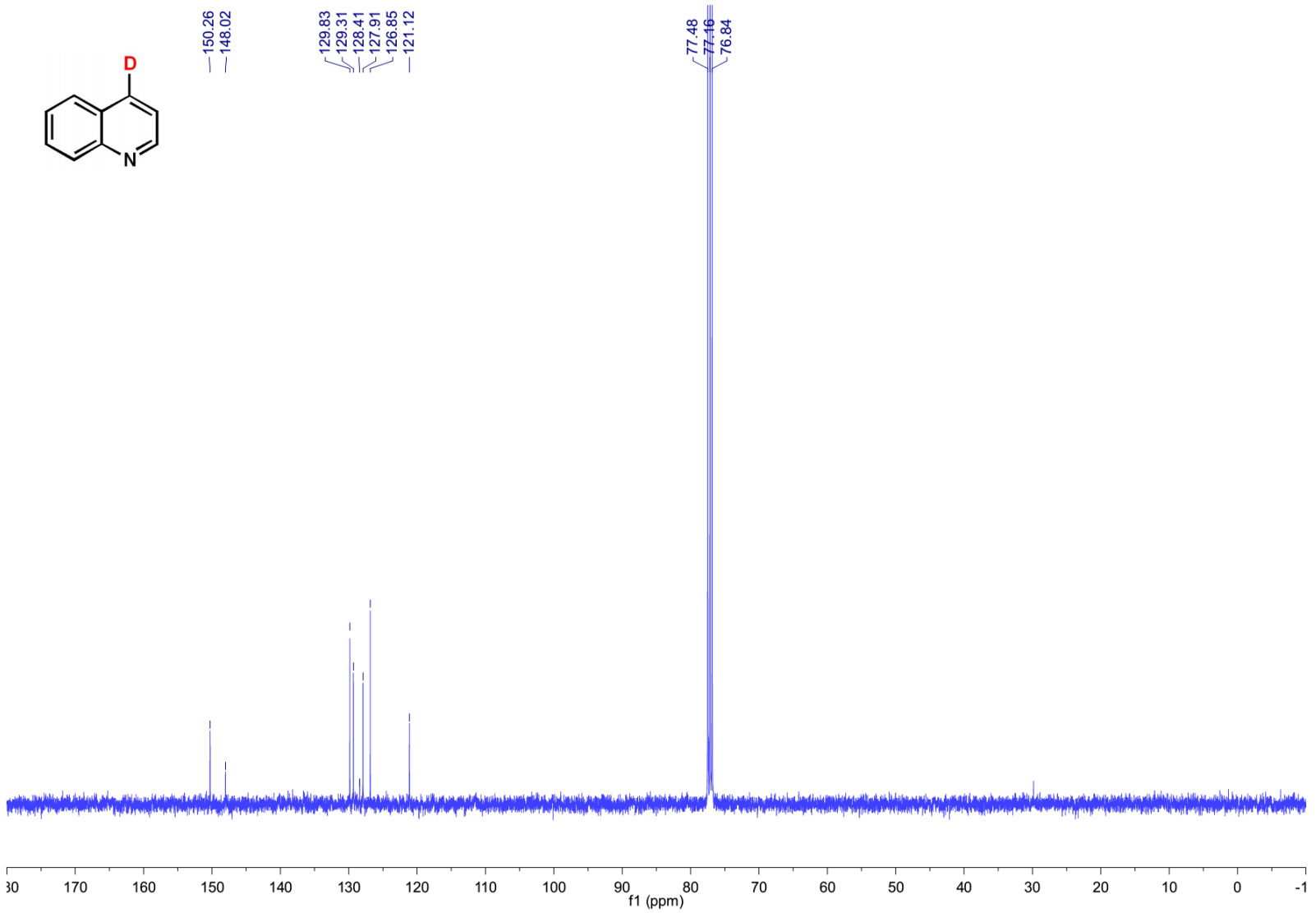


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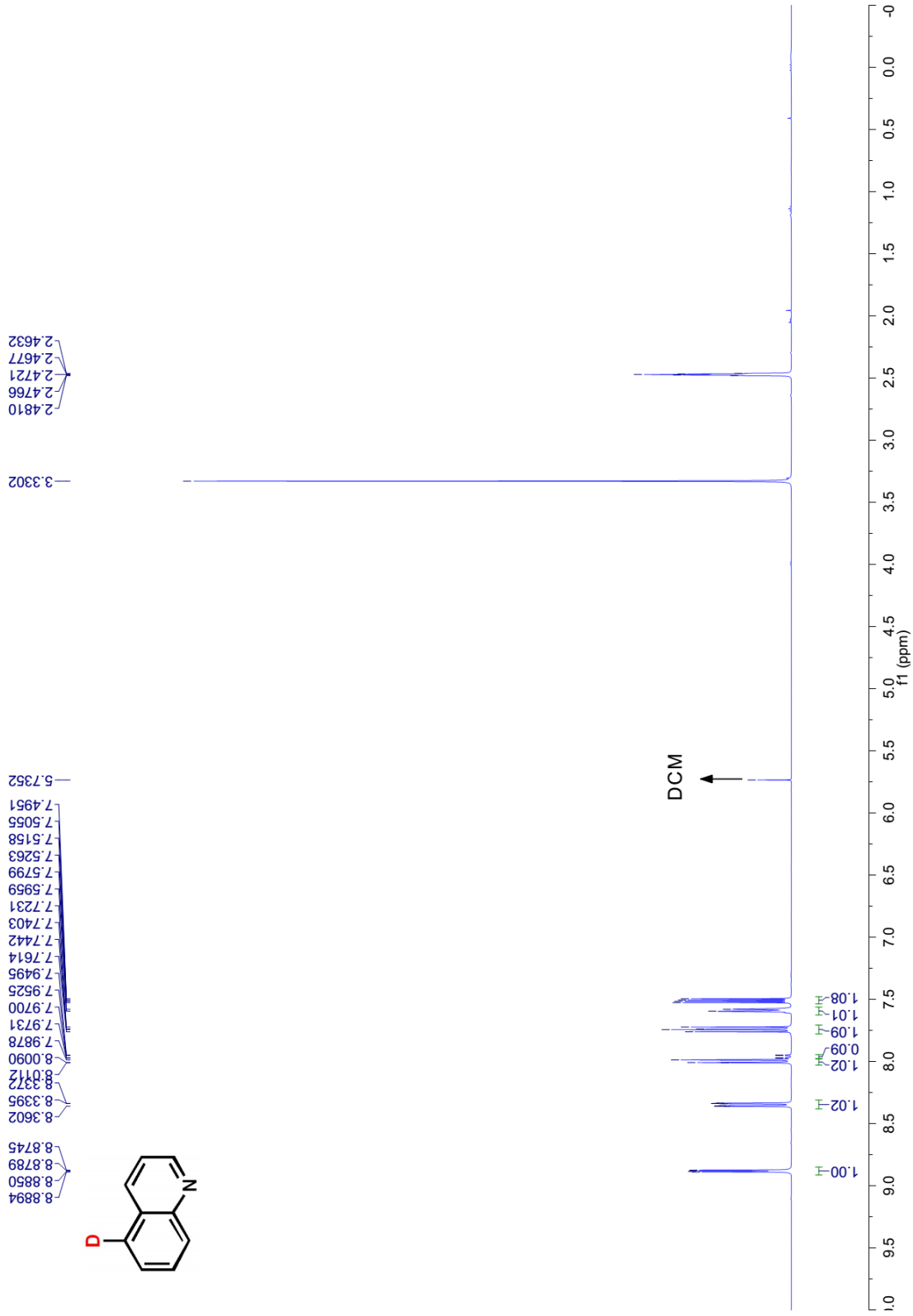
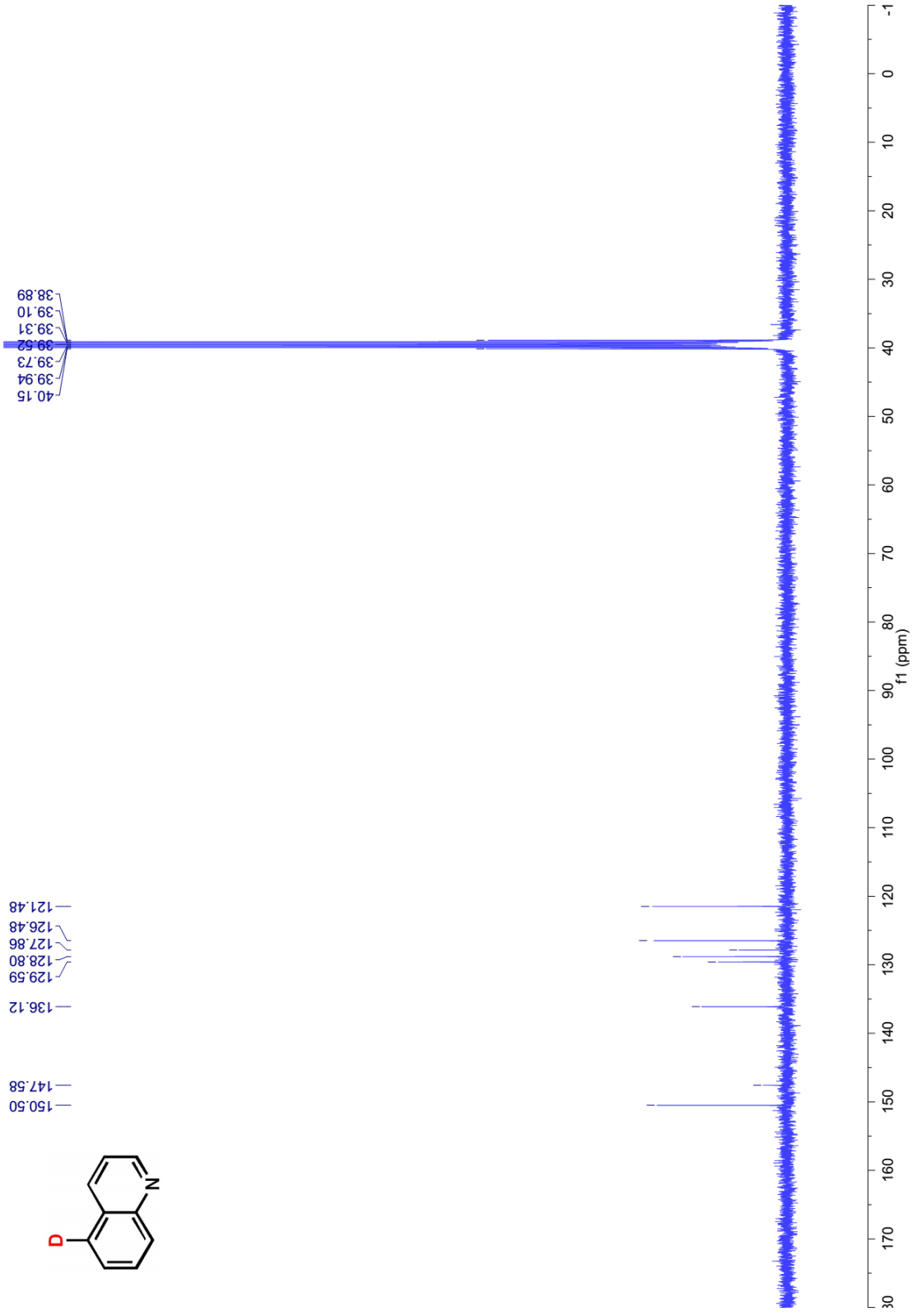
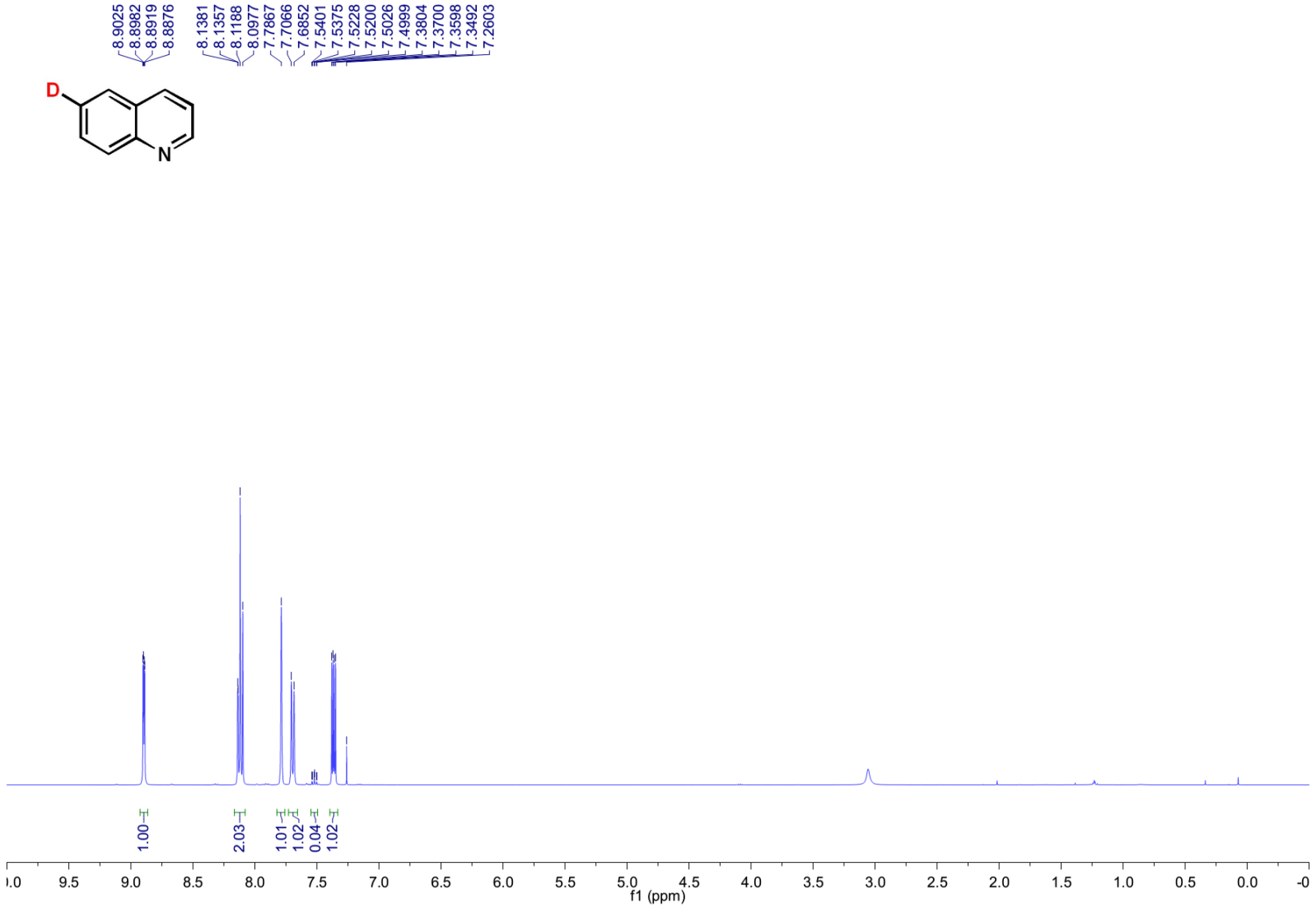


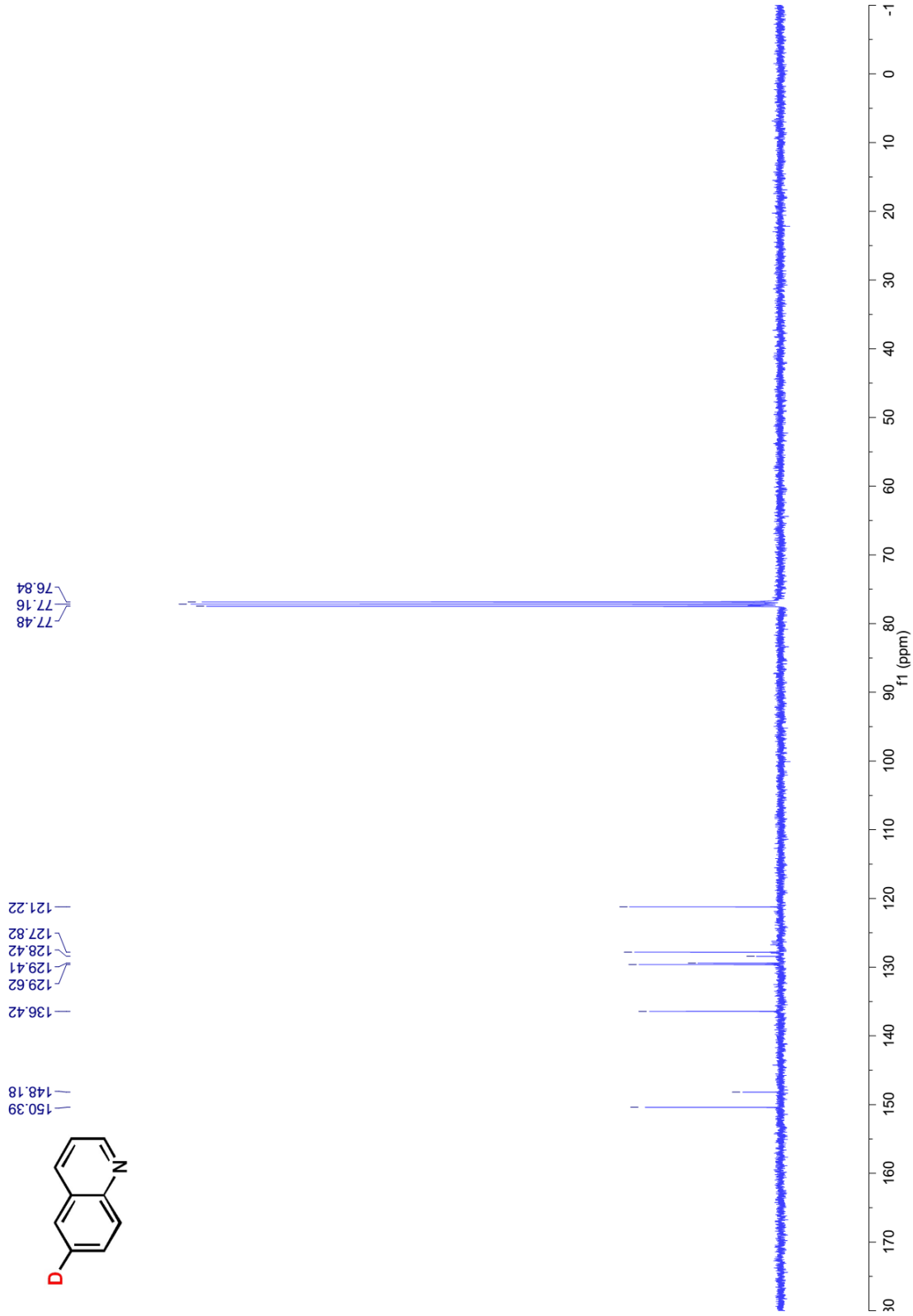

$^1$H NMR (400 MHz, DMSO-$d_6$) of ***3f***



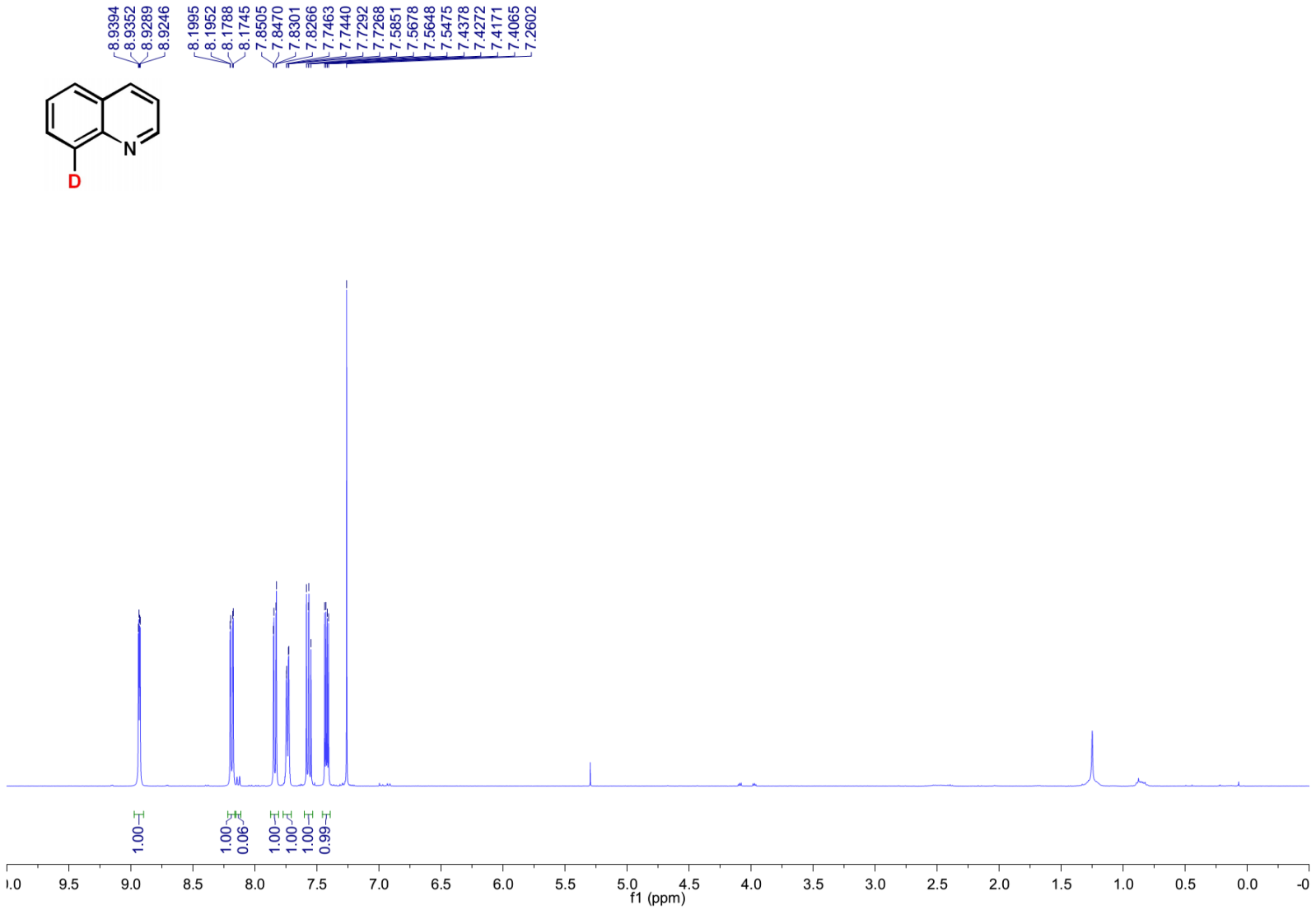

$^{13}$C NMR (100 MHz, DMSO-$d_6$) of ***3f***




$^{1}$H NMR (400 MHz, $CDCl_3$) of ***3g***




$^{13}$C NMR (100 MHz, $CDCl_3$) of ***3g***

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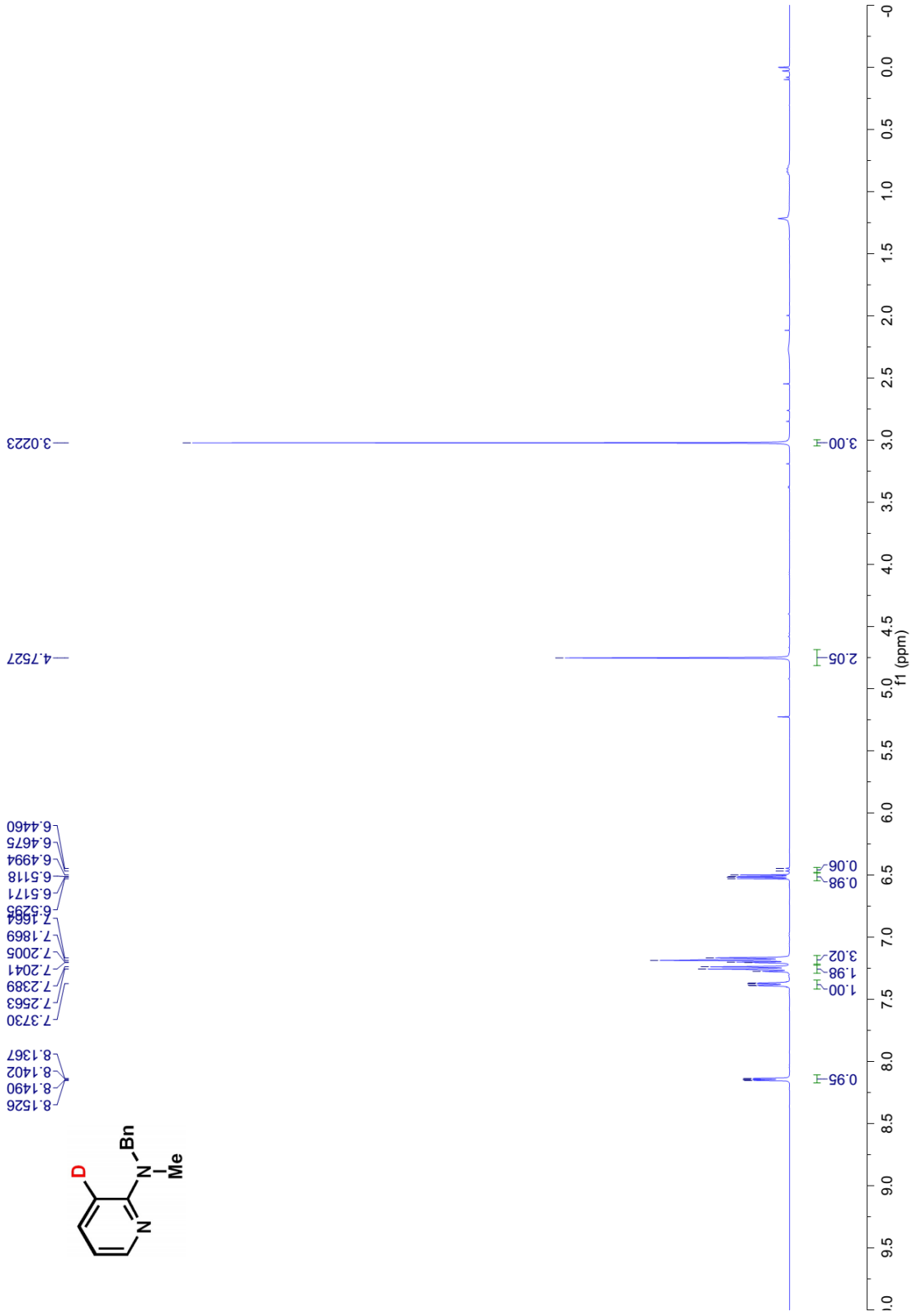
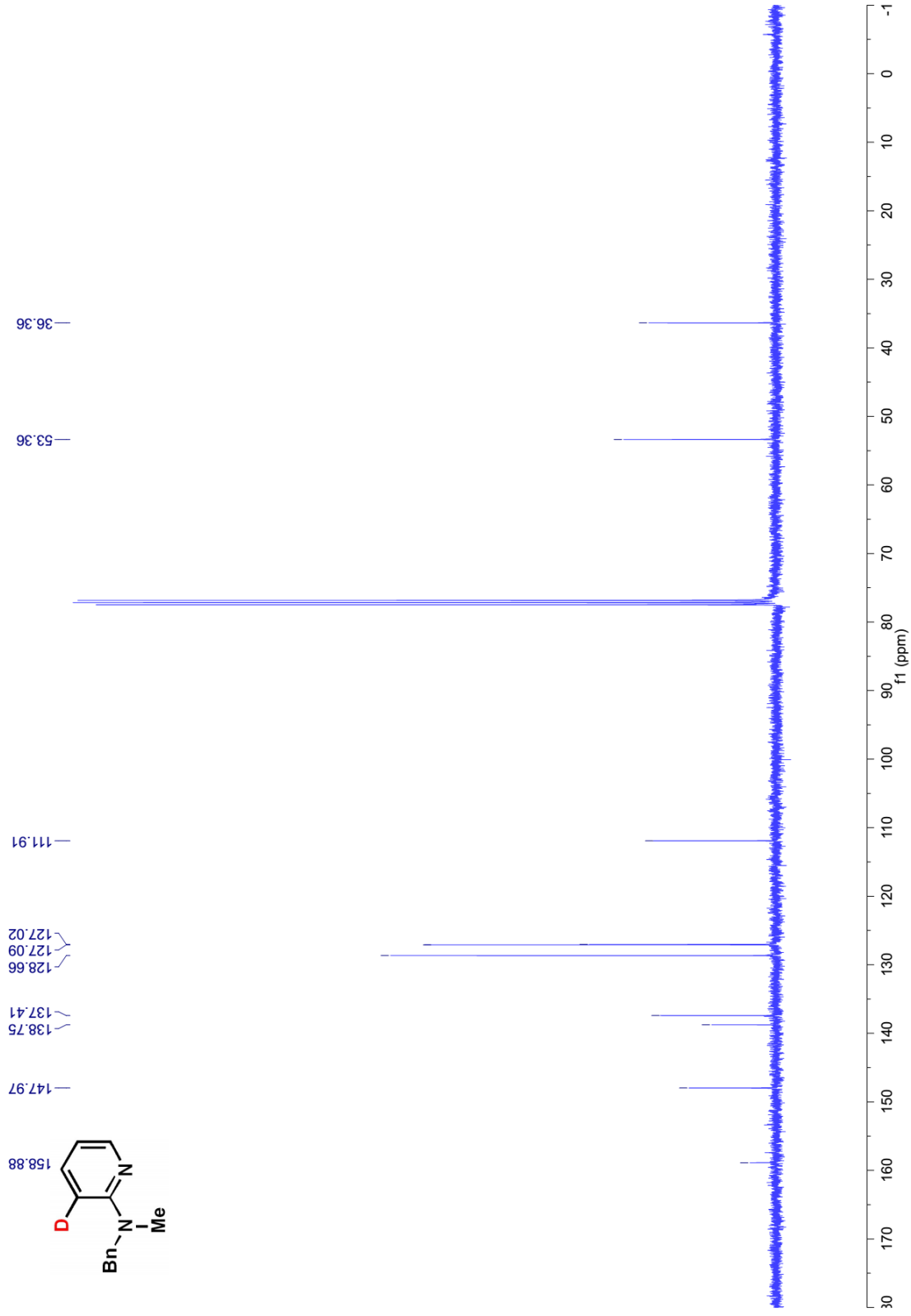
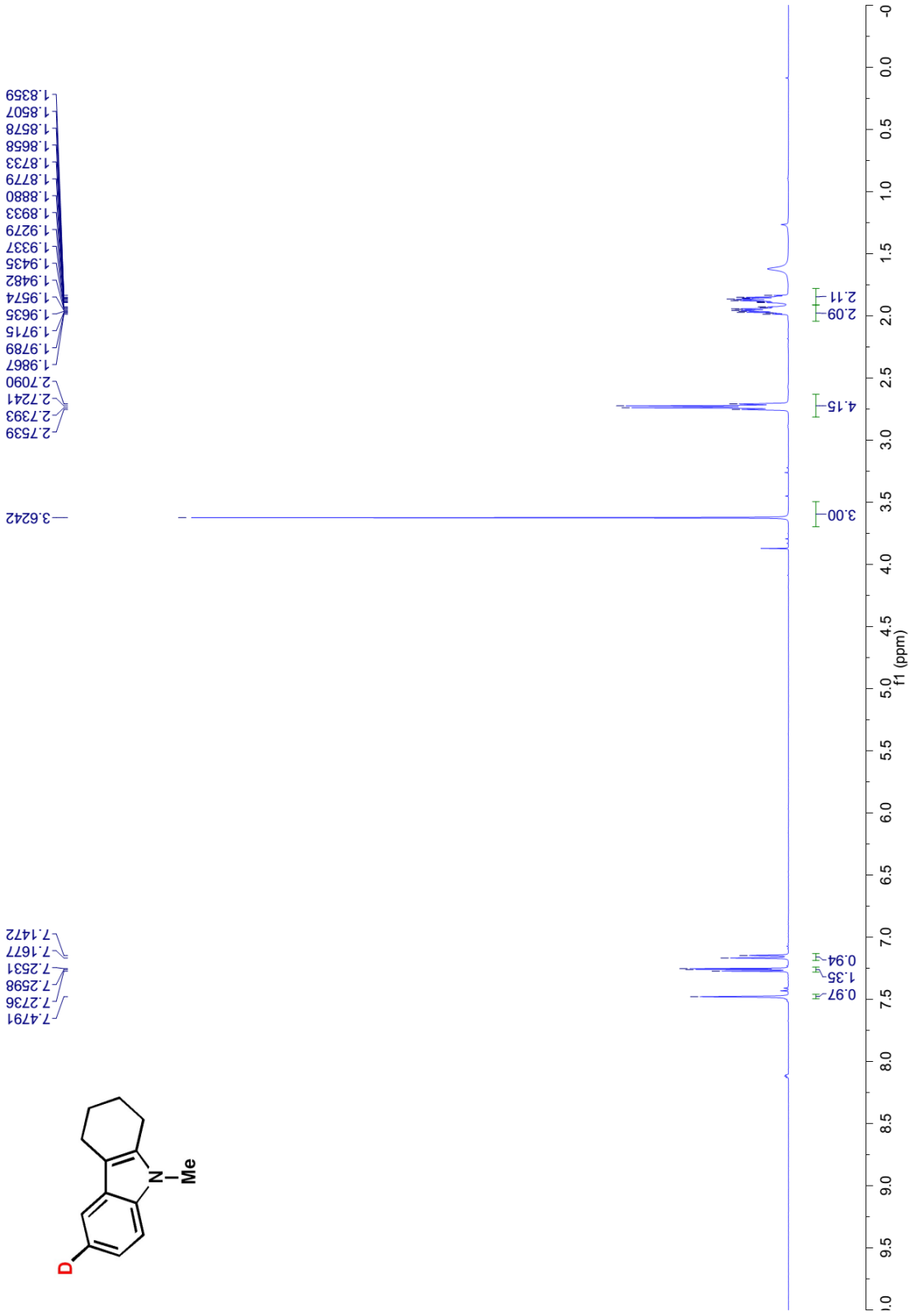


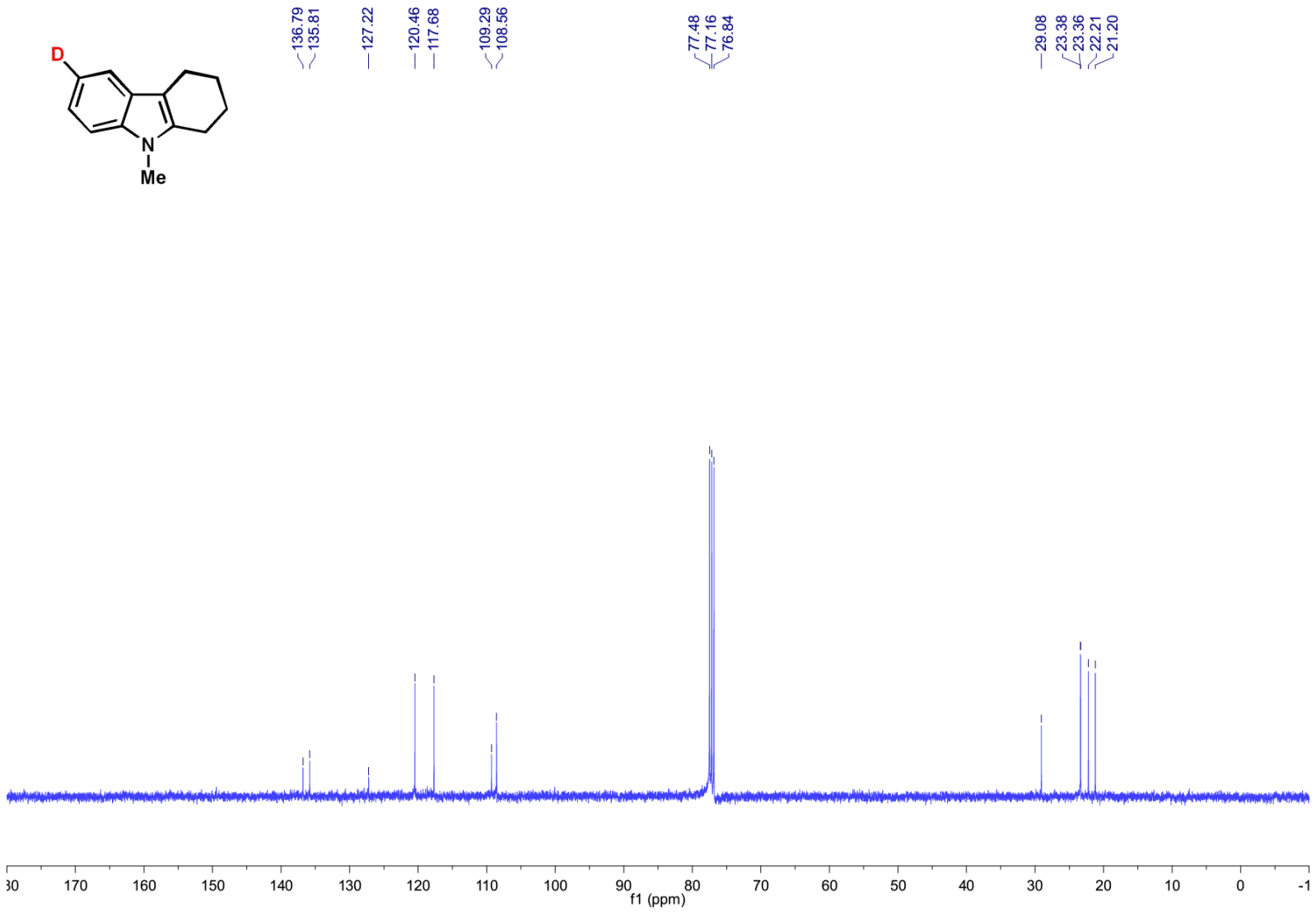

$^1$H NMR (400 MHz, $CDCl_3$) of ***4a***




$^{13}$C NMR (100 MHz, $CDCl_3$) of ***4a***




$^1$H NMR (400 MHz, $CDCl_3$) of ***4b***

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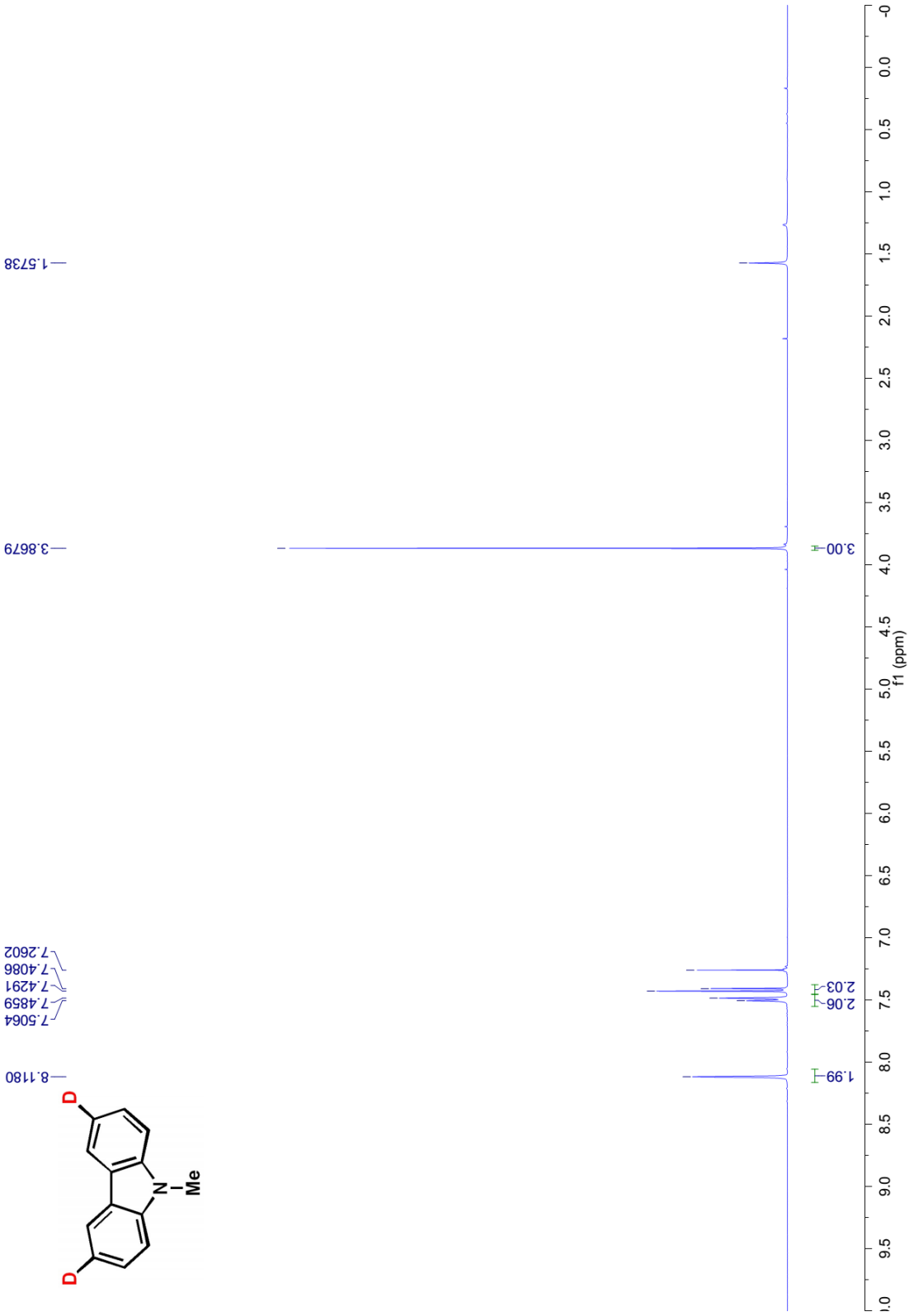


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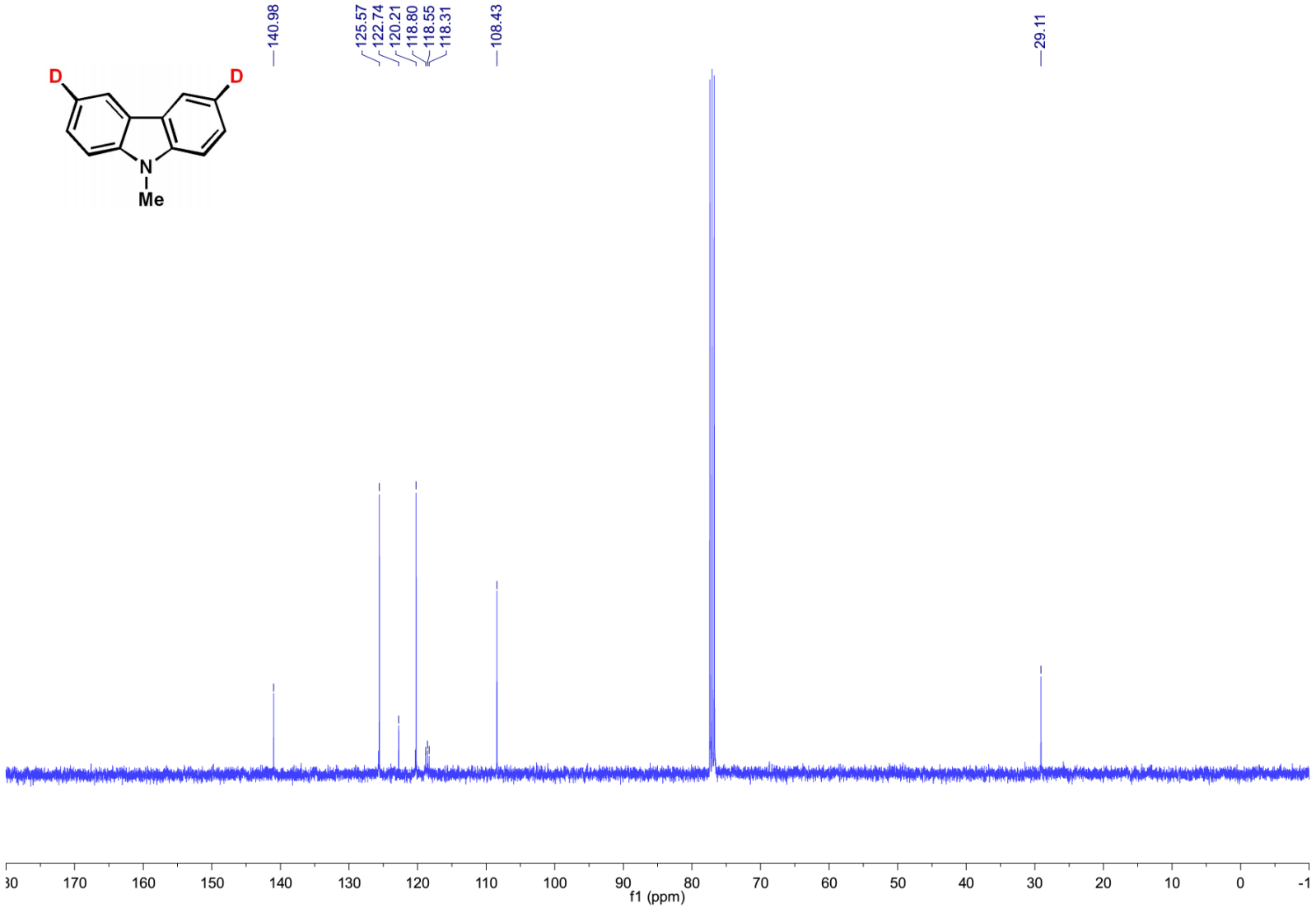
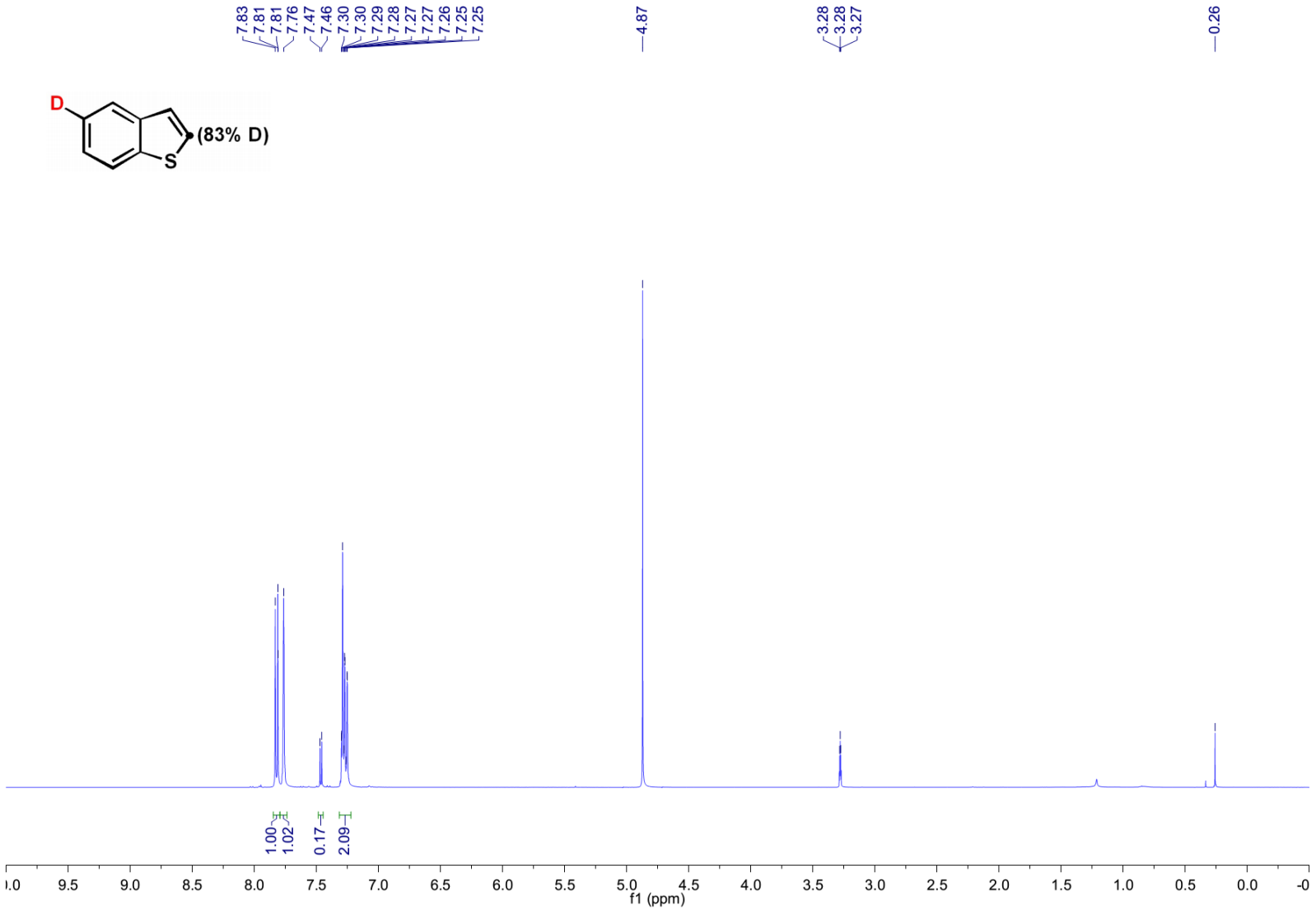
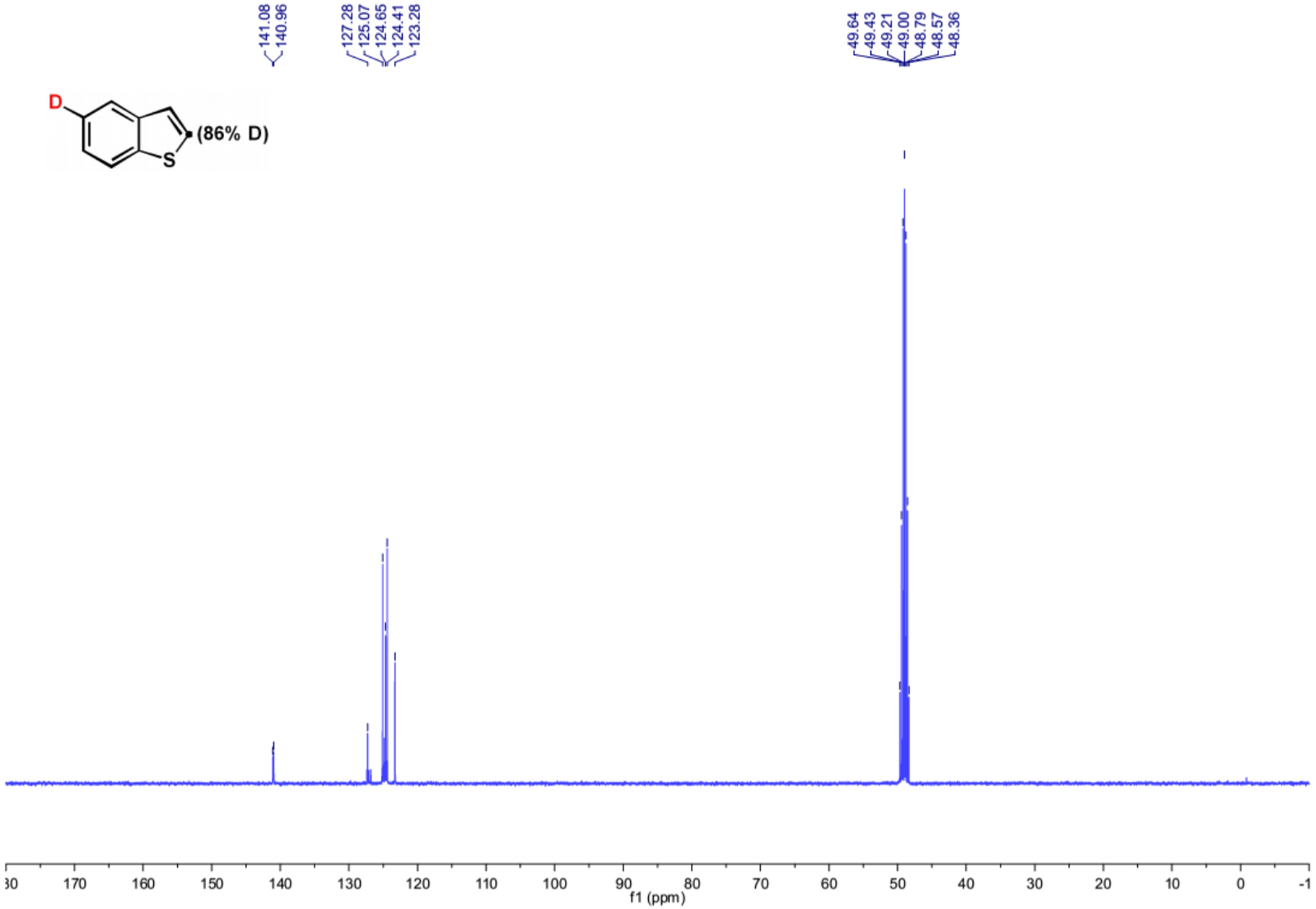



$^{13}$C NMR (100 MHz, $CDCl_3$) of ***4c***




$^1$H NMR (400 MHz, $CD_3OD$) of ***4d***

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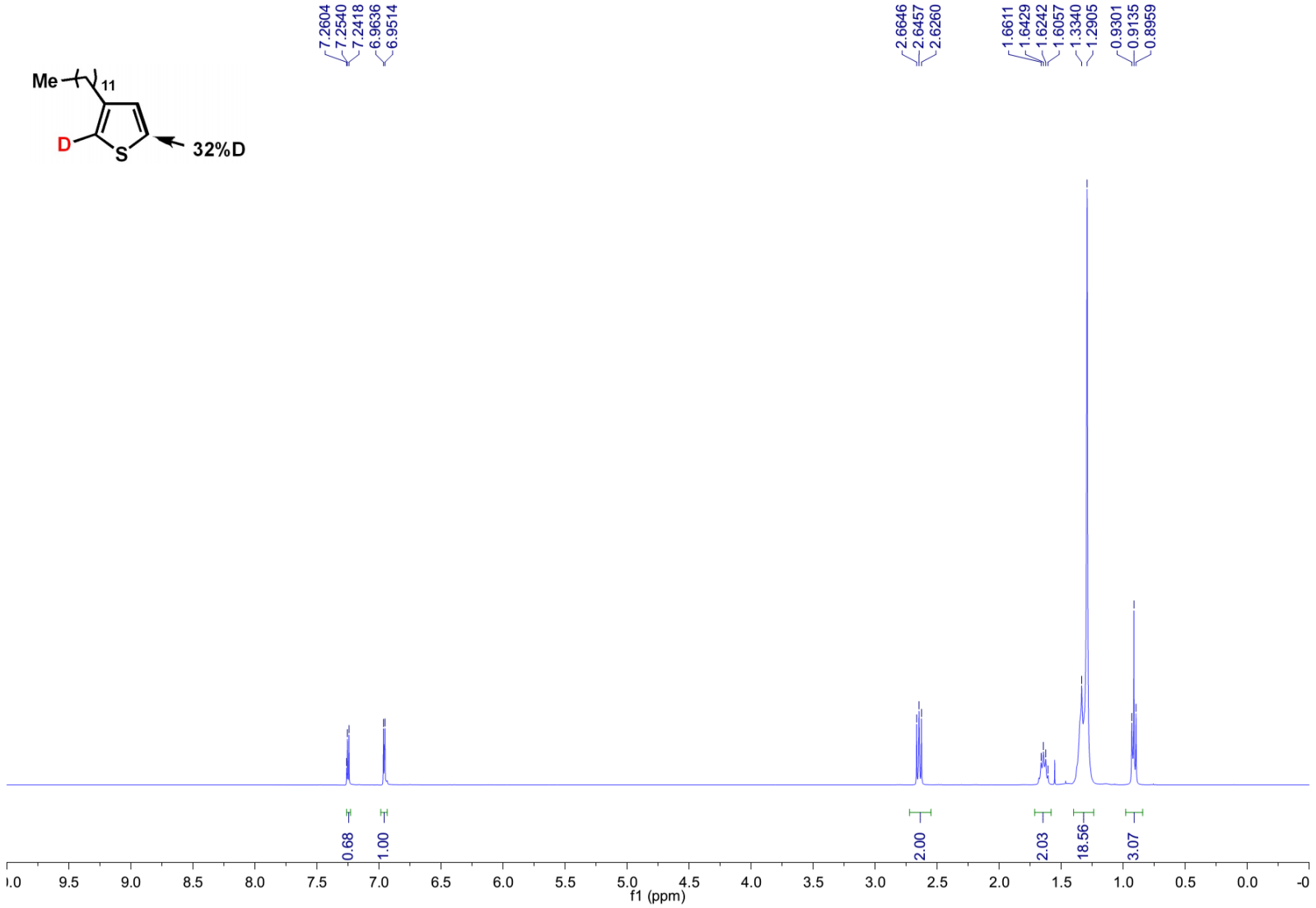
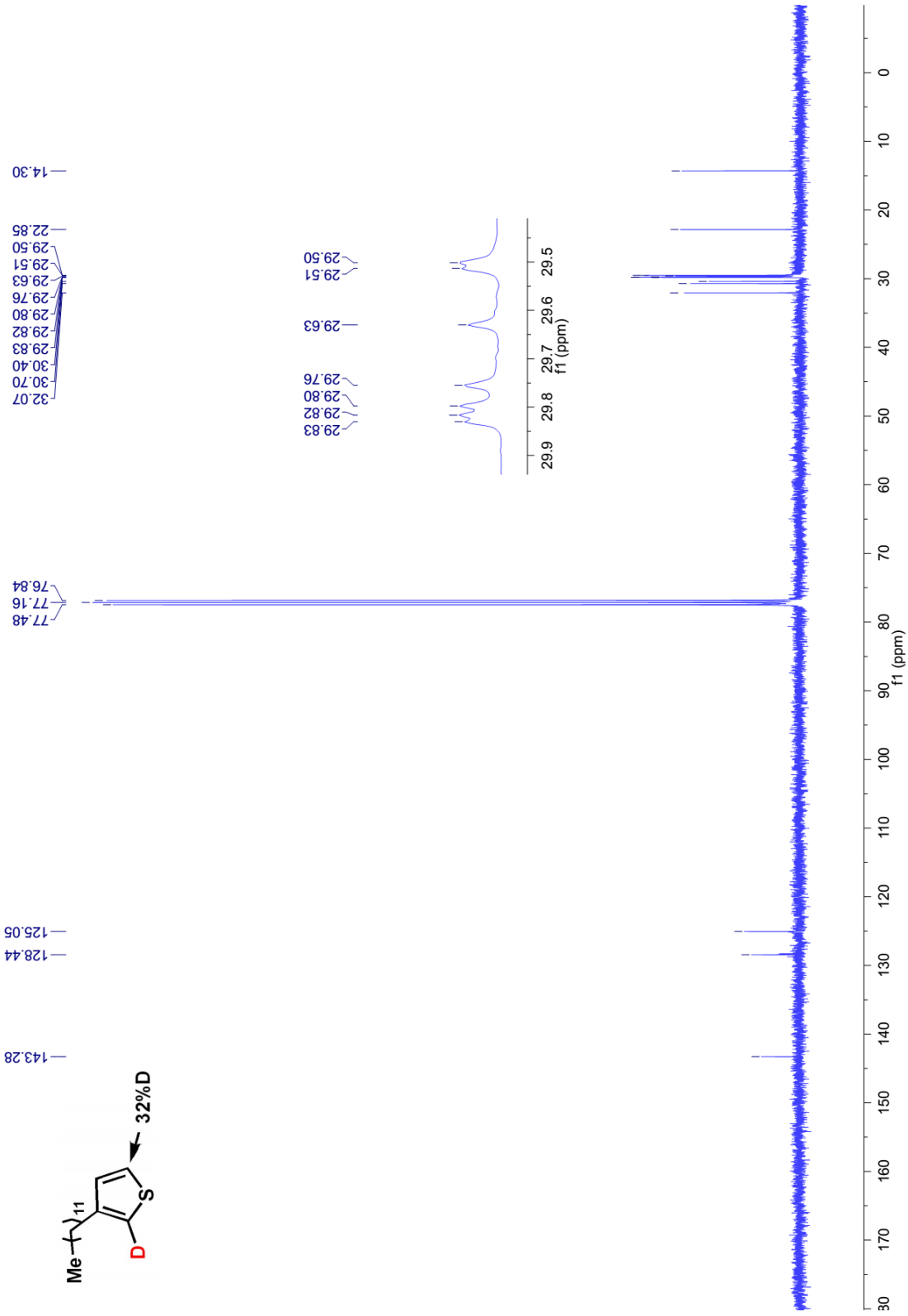
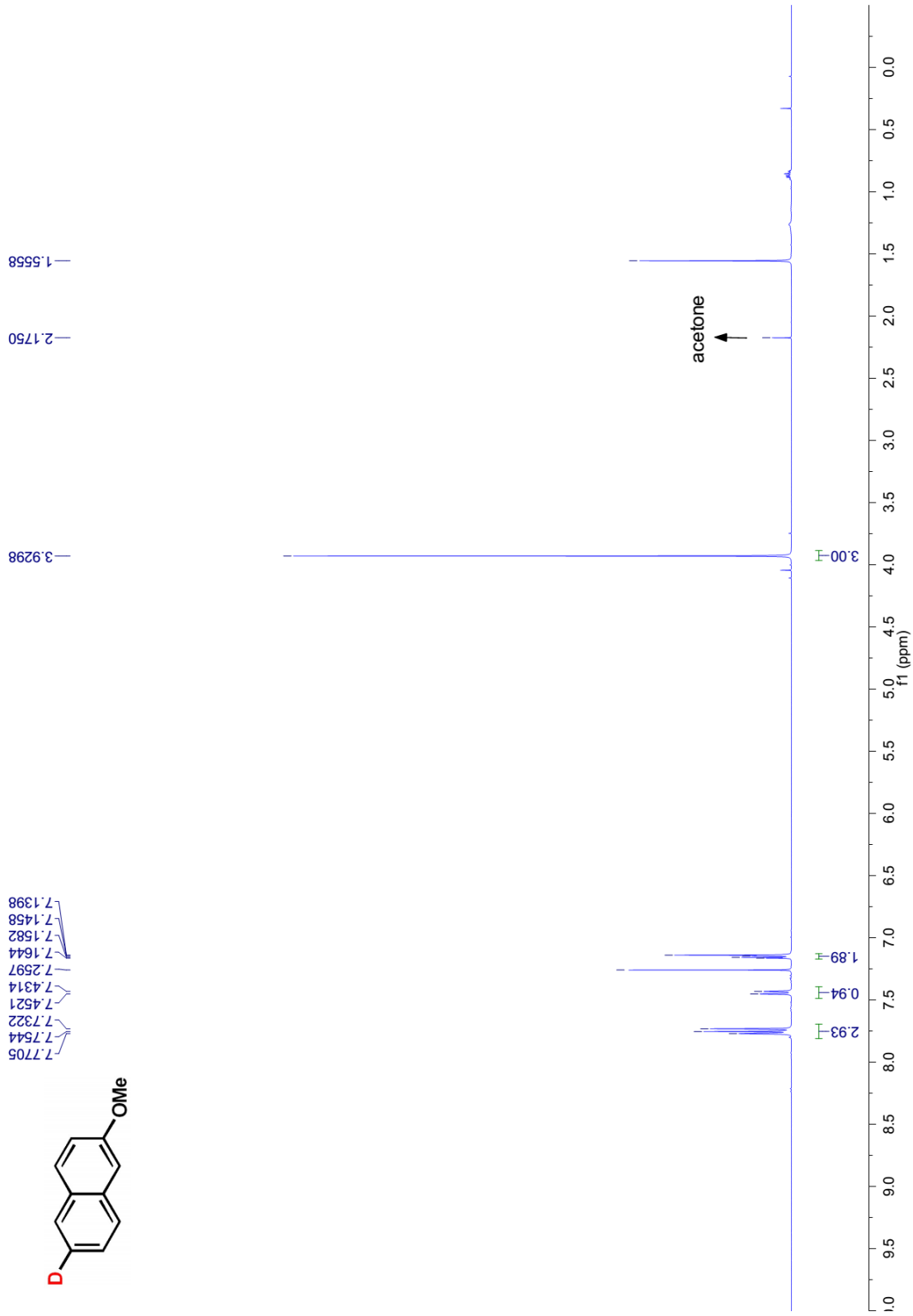


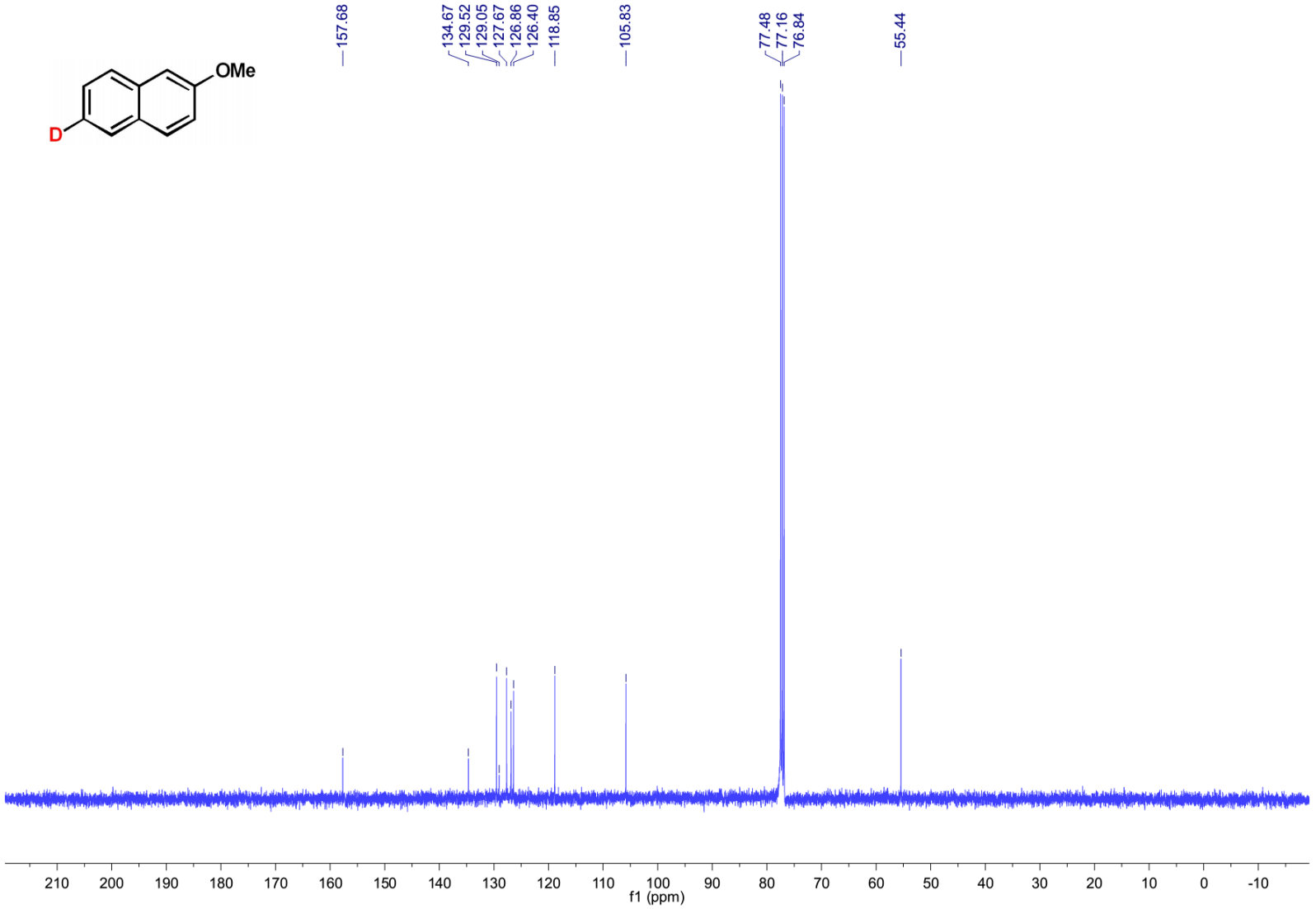

$^{1}$H NMR (400 MHz, $CDCl_3$) of ***4e***



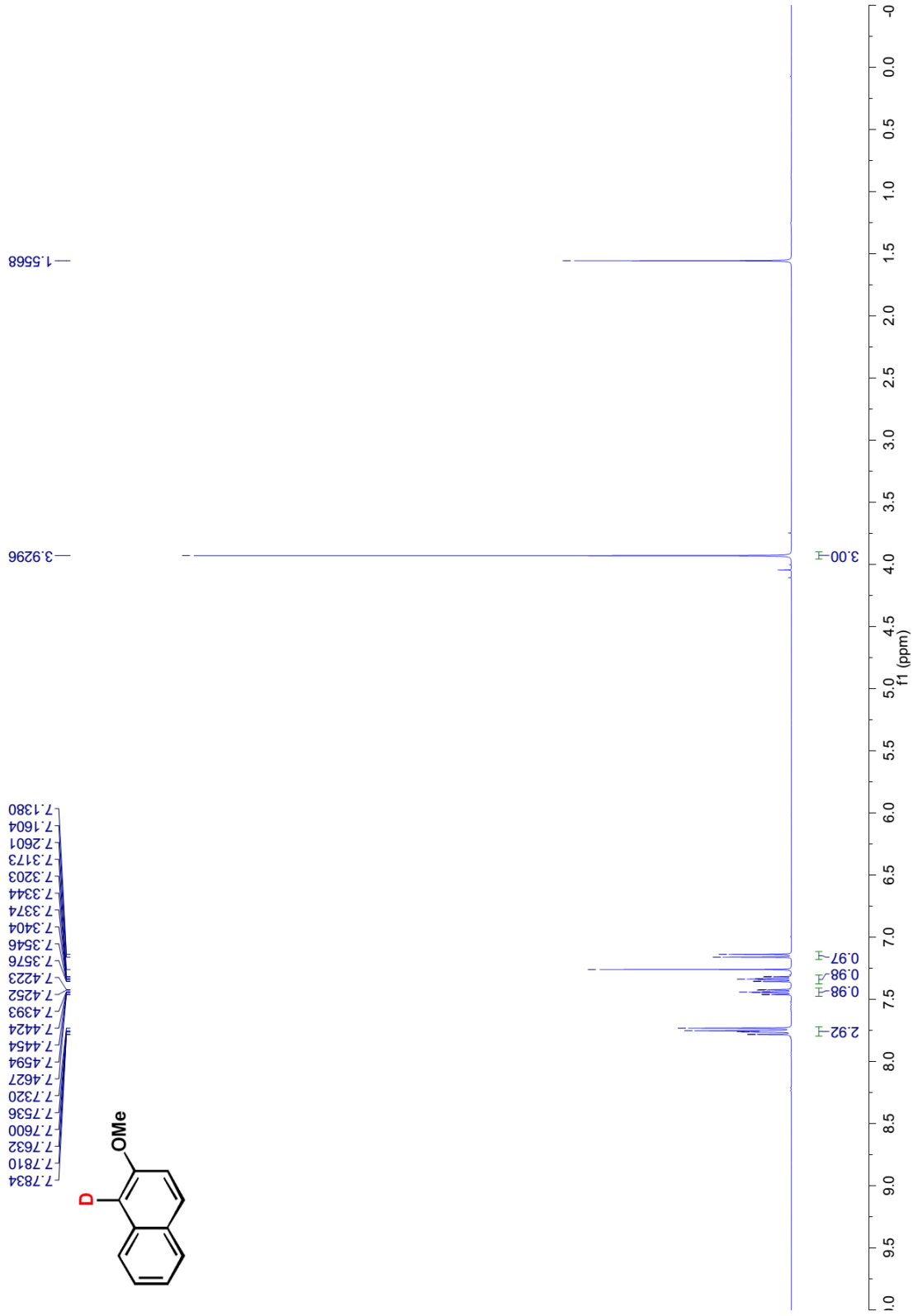

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***4e***



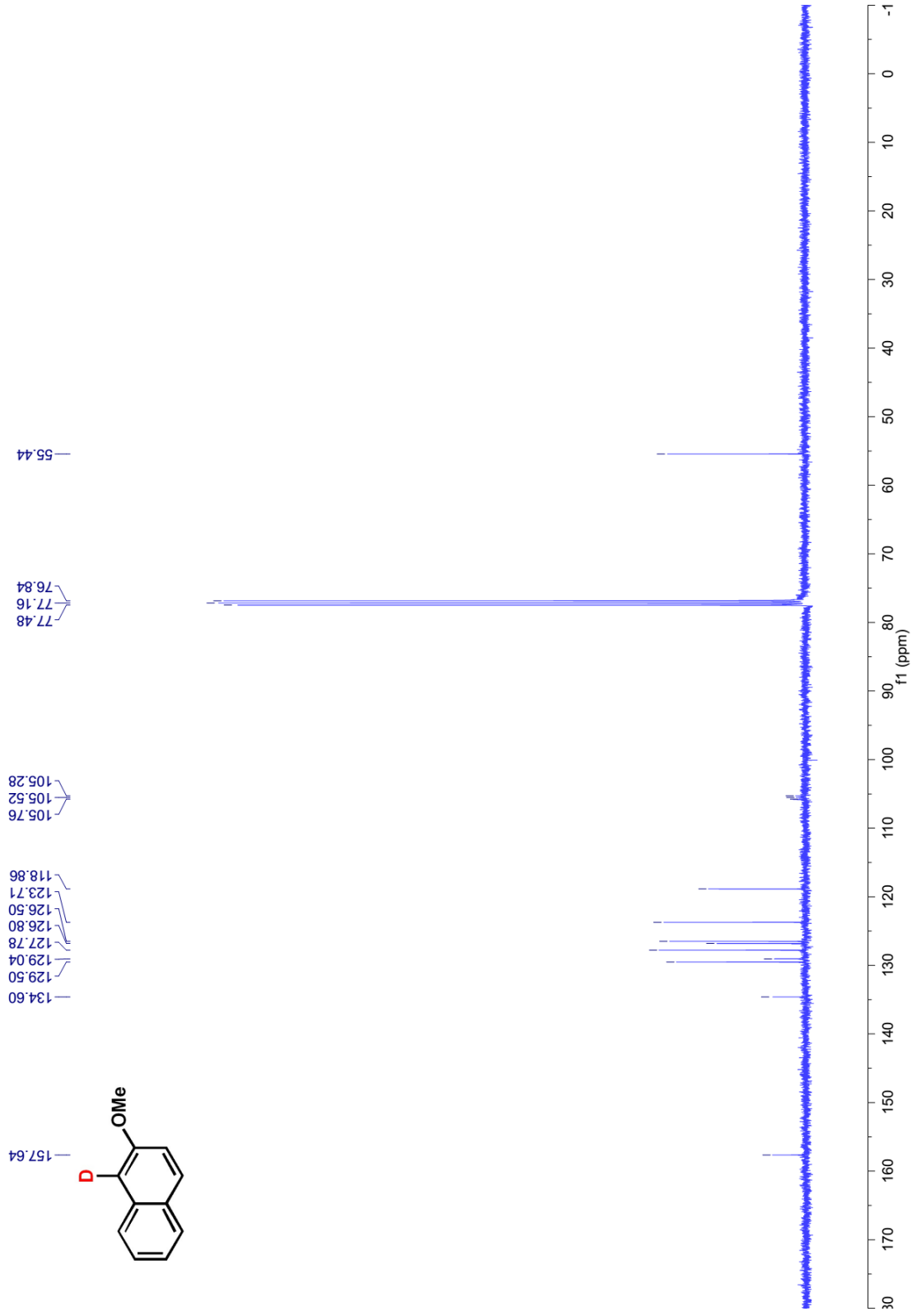

$^1$H NMR (400 MHz, $CDCl_3$) of ***4f***




$^{13}$C NMR (100 MHz, $CDCl_3$) of ***4f***




$^1$H NMR (400 MHz, $CDCl_3$) of ***4g***

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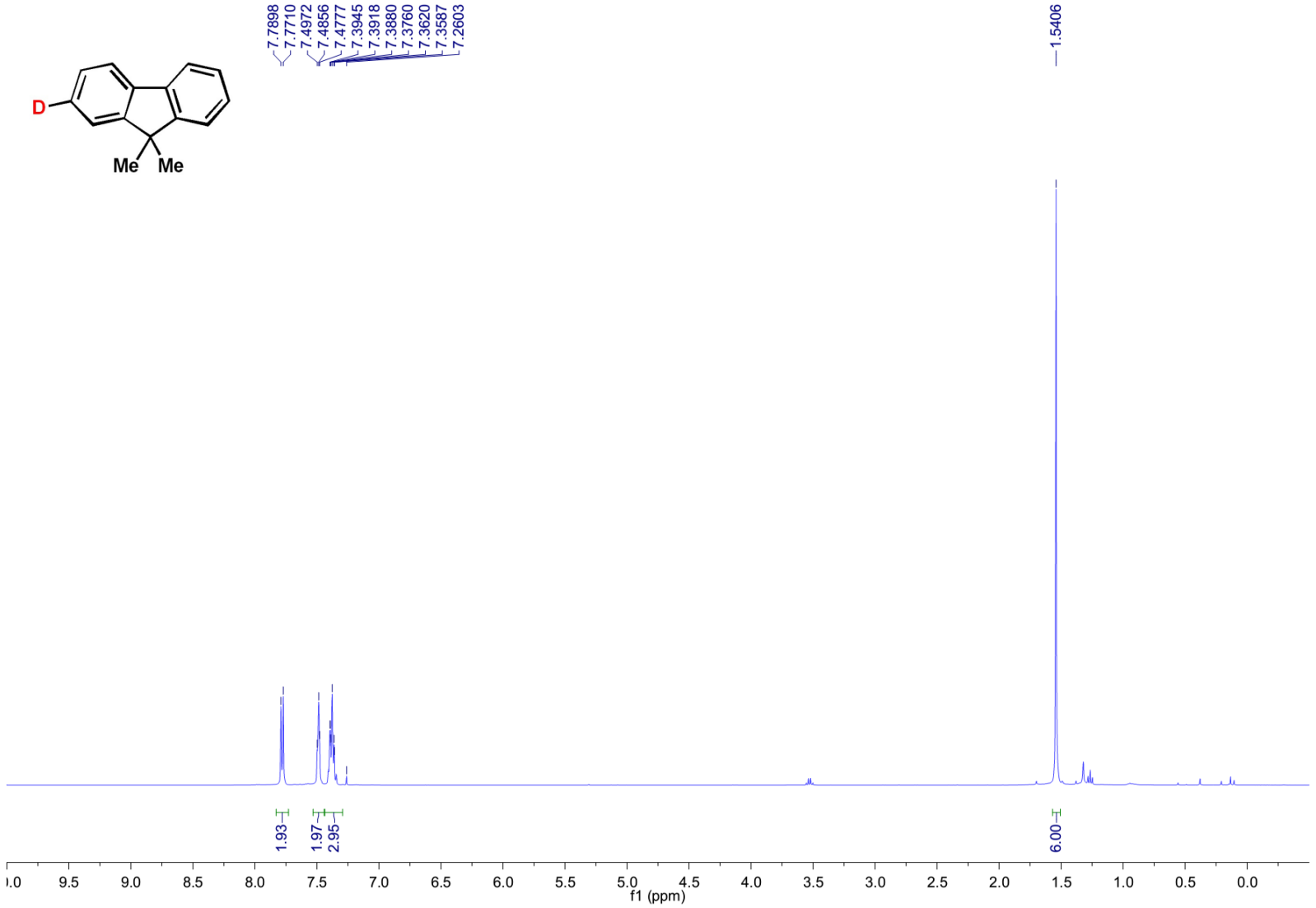
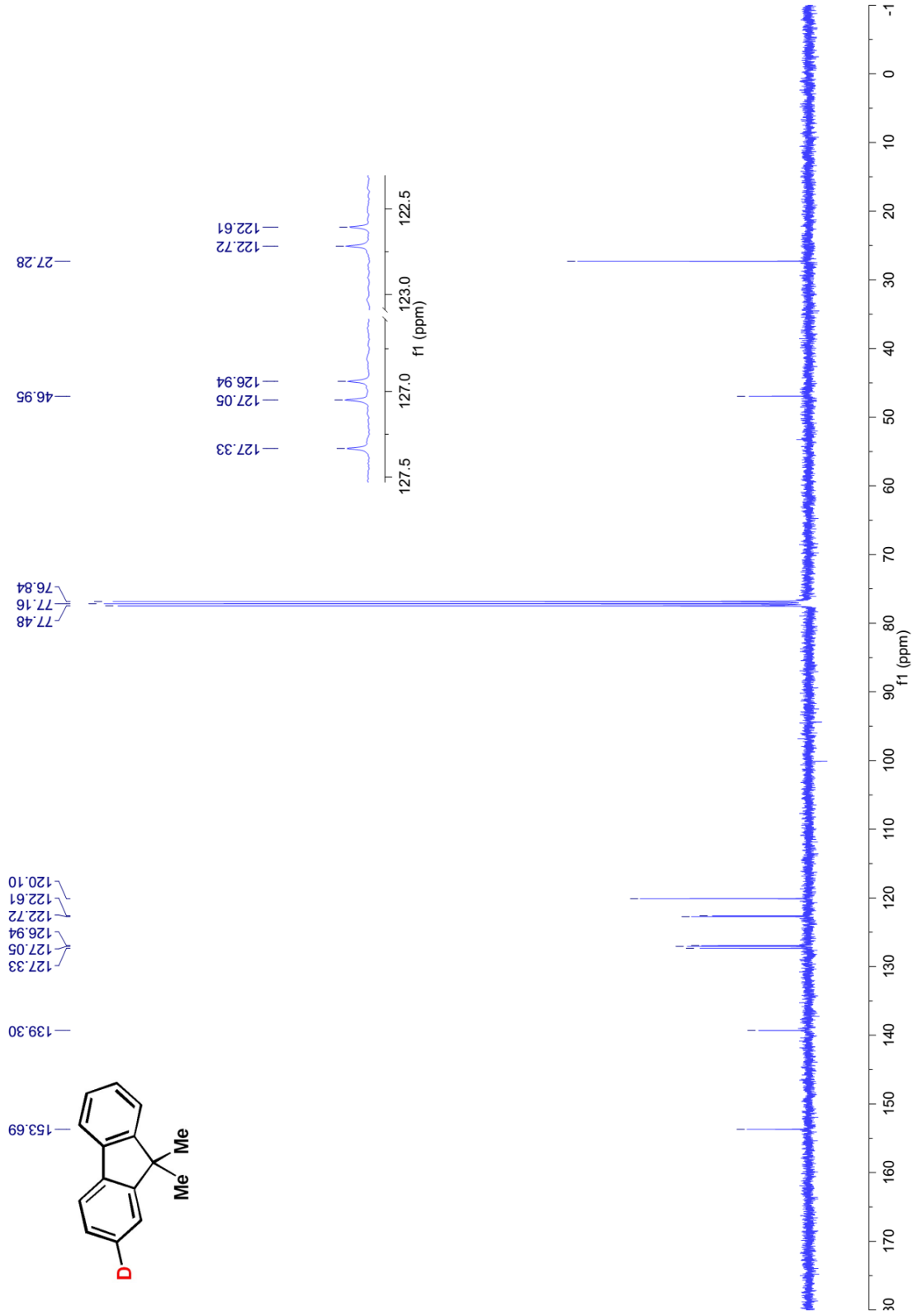
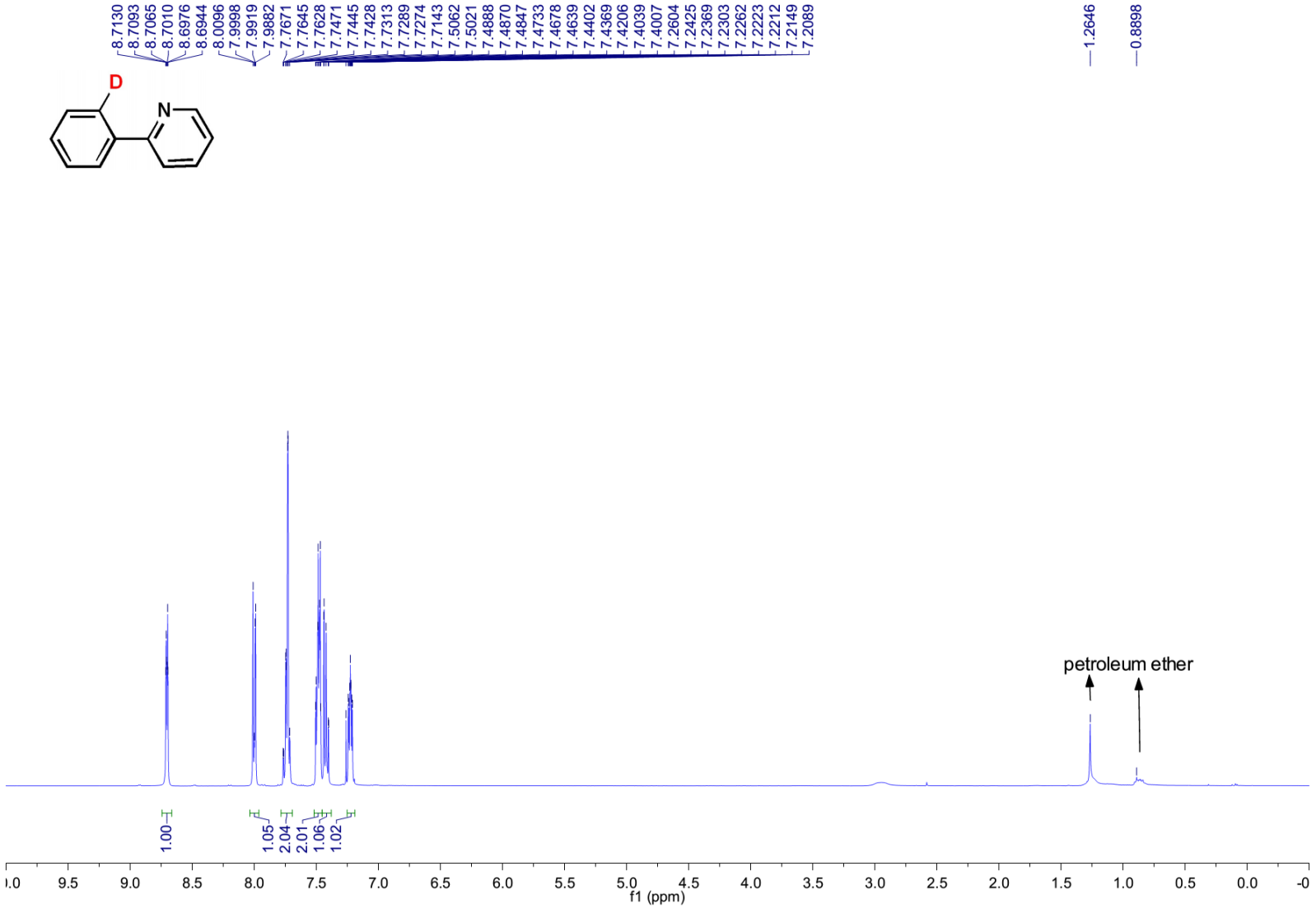


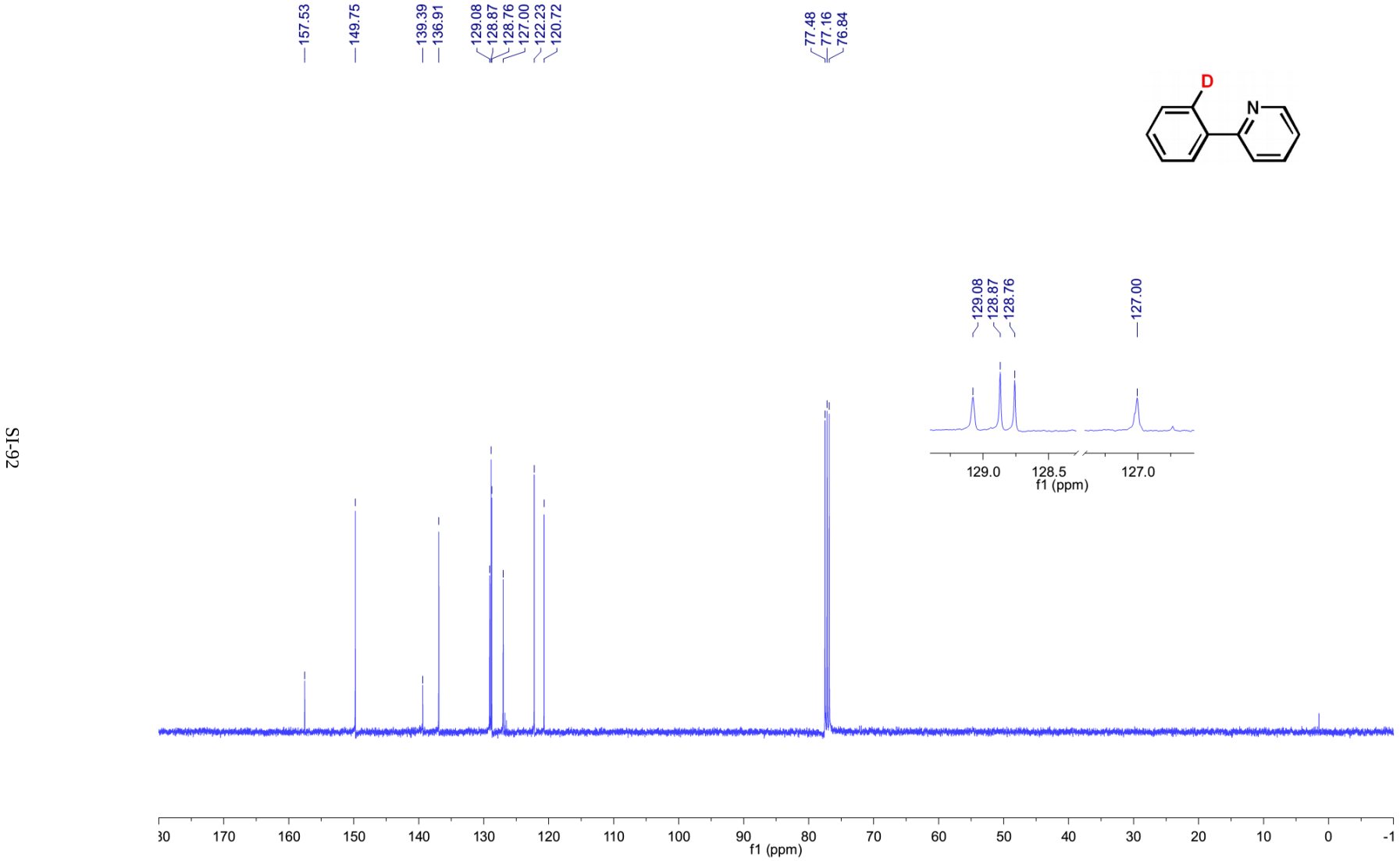

$^{1}$H NMR (400 MHz, $CDCl_3$) of ***4h***



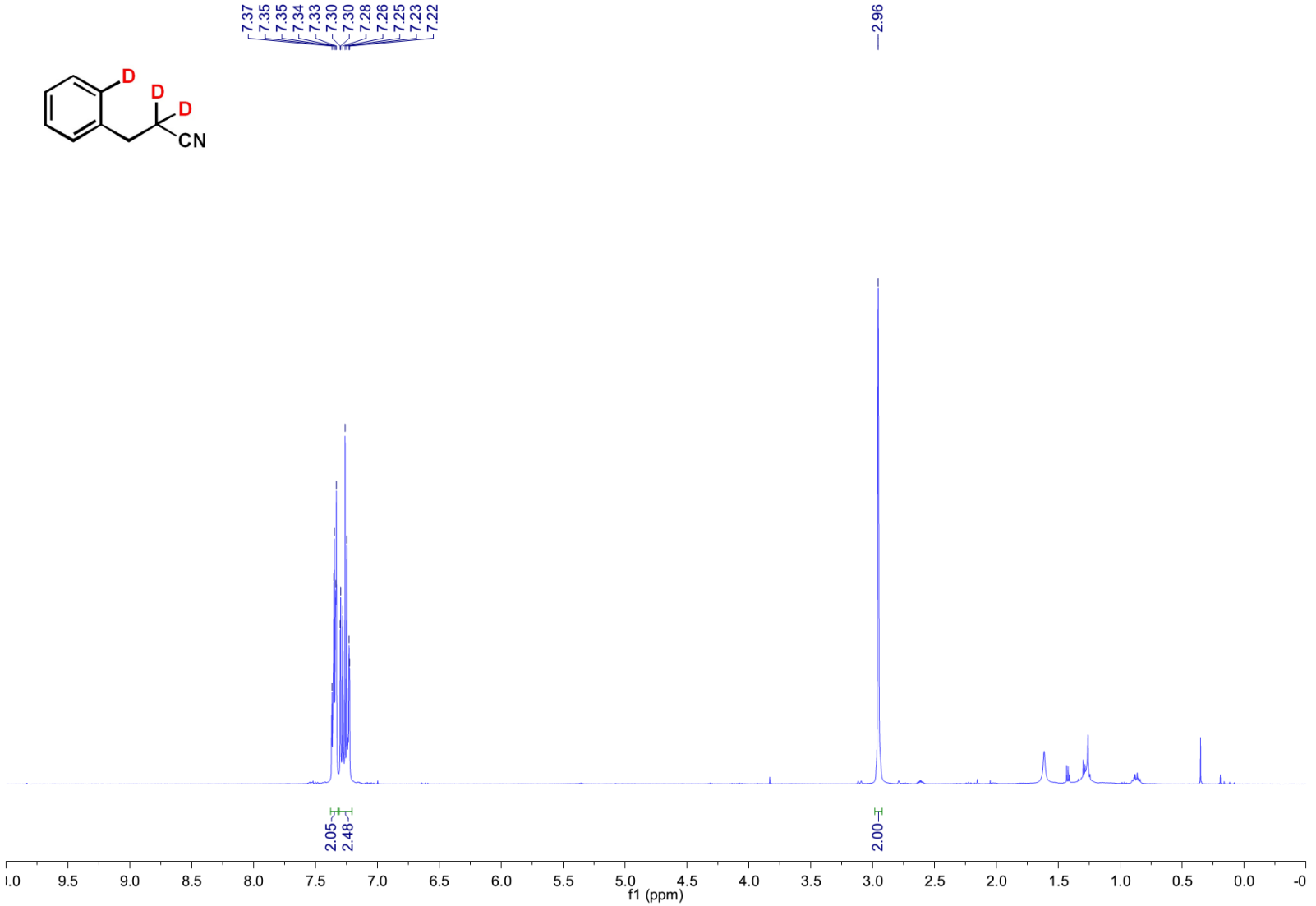

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***4h***



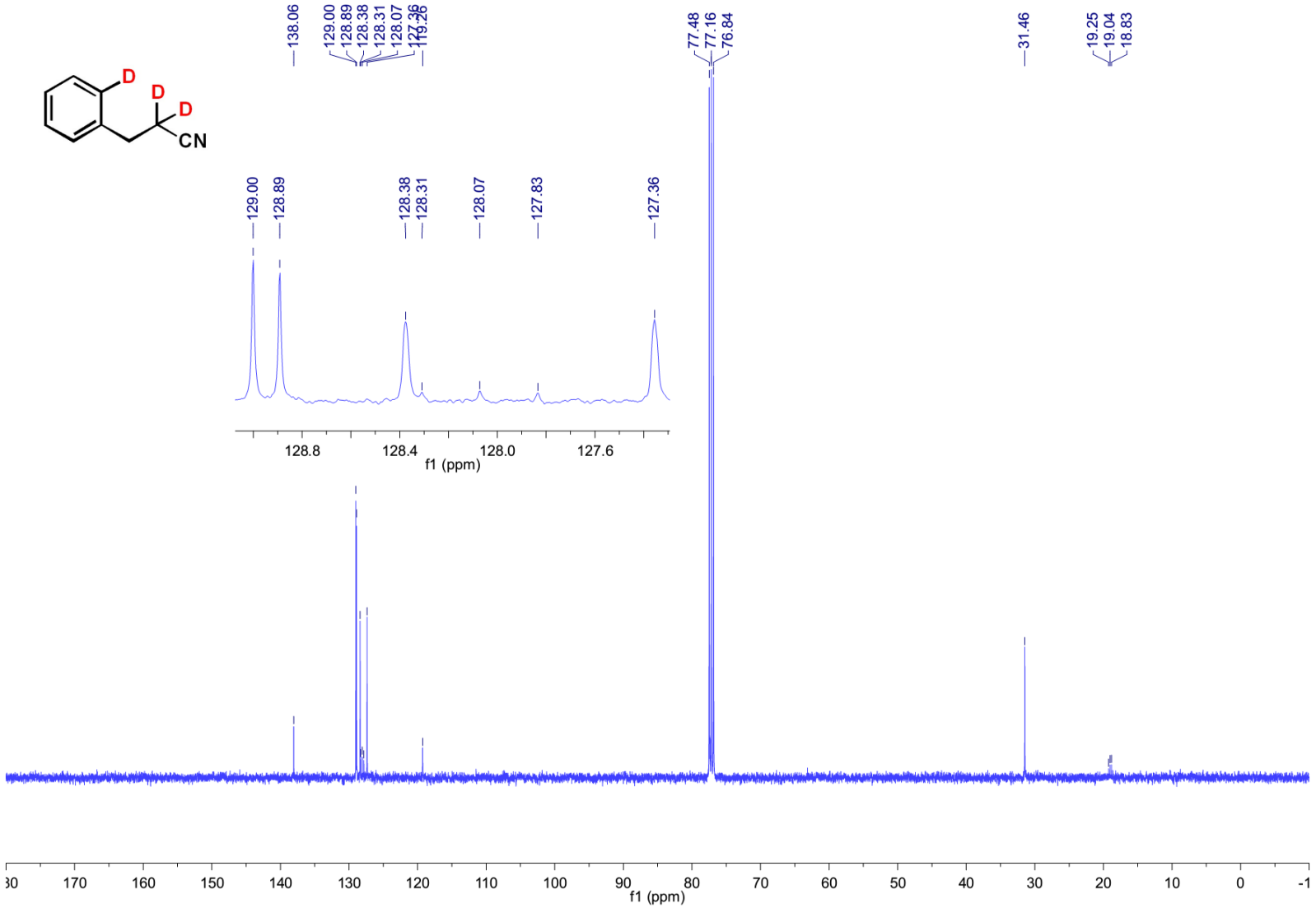

$^{1}$H NMR (400 MHz, $CDCl_3$) of ***4i***



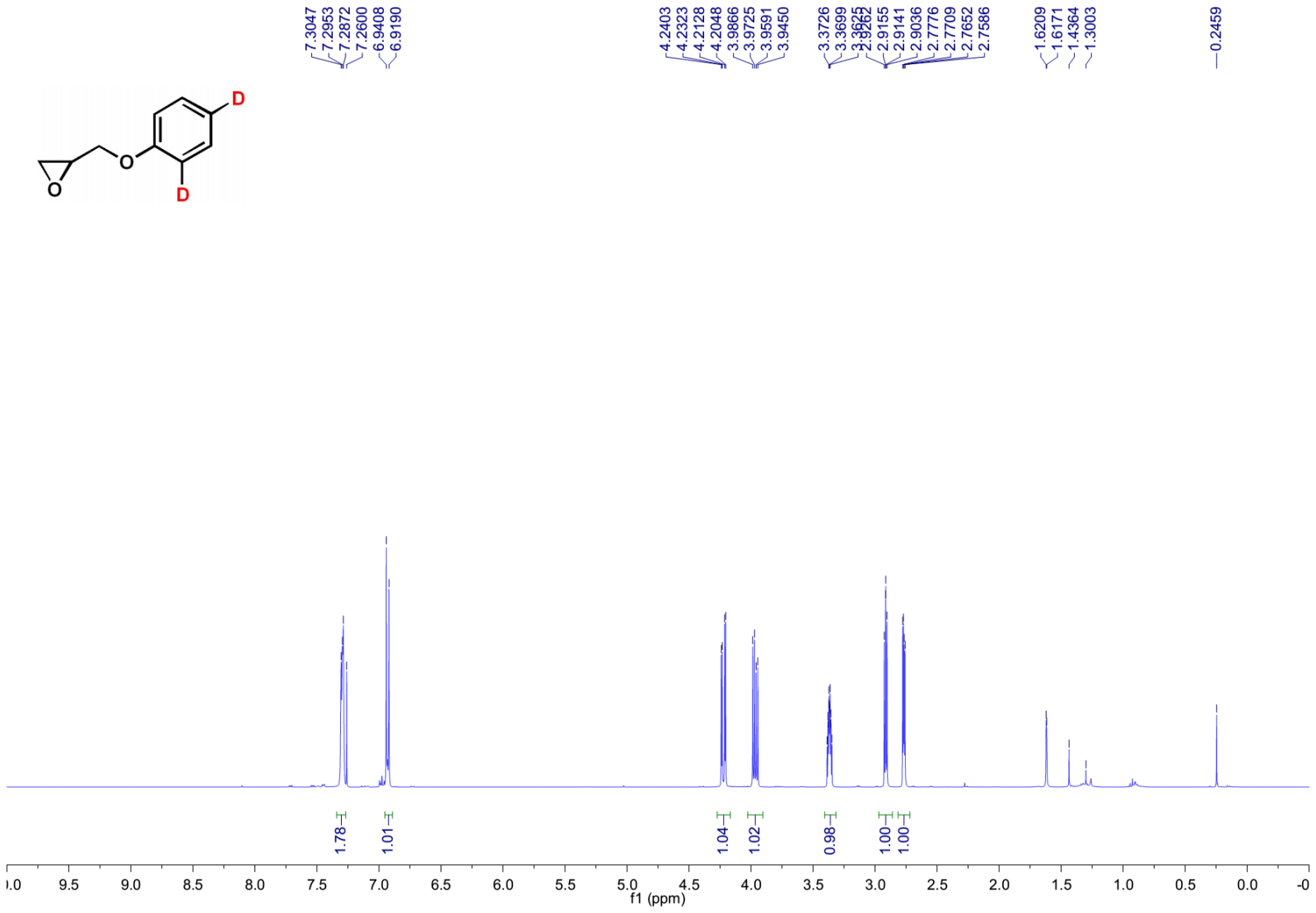

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***4i***



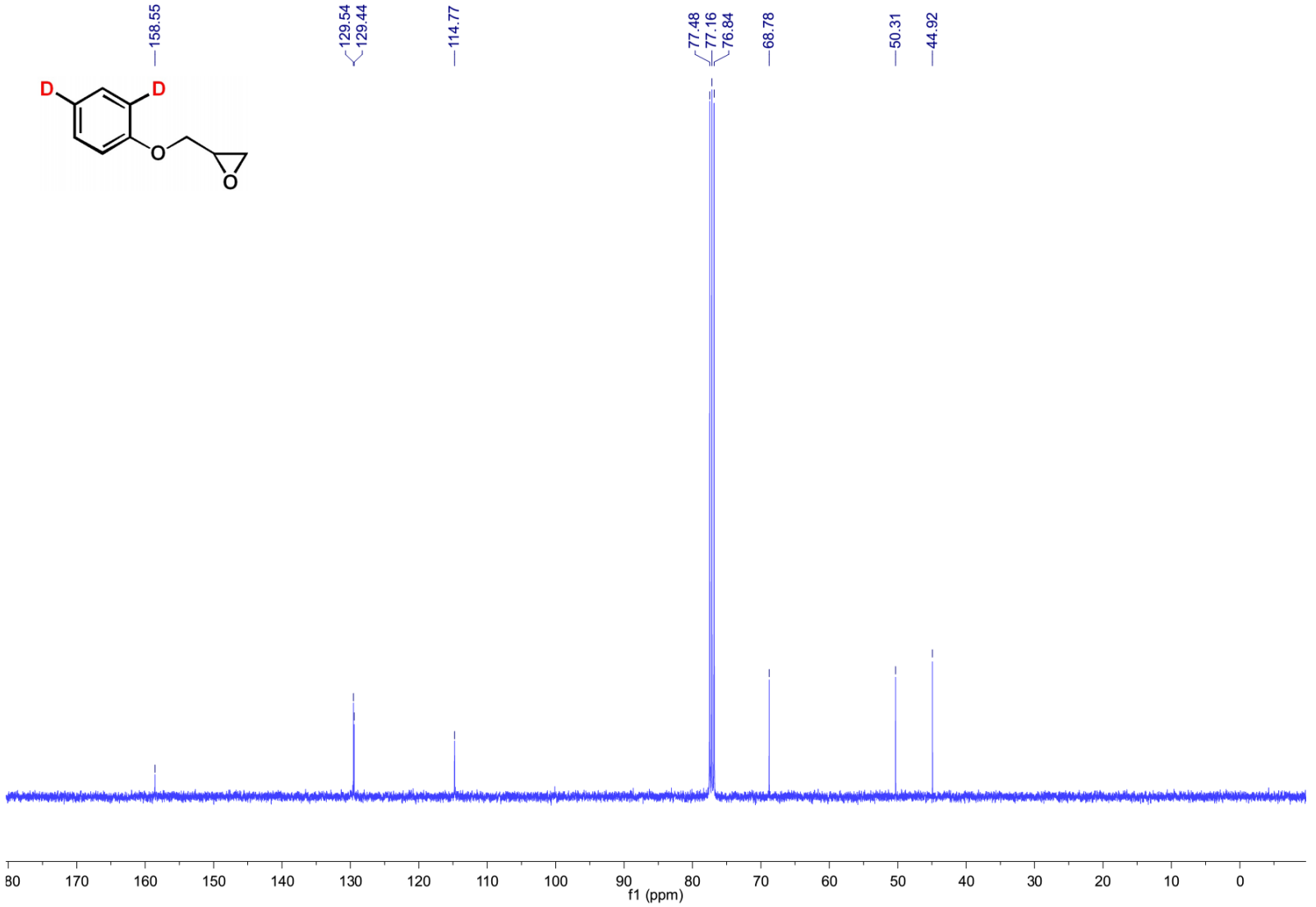

$^{1}$H NMR (400 MHz, $CDCl_3$) of ***4j***



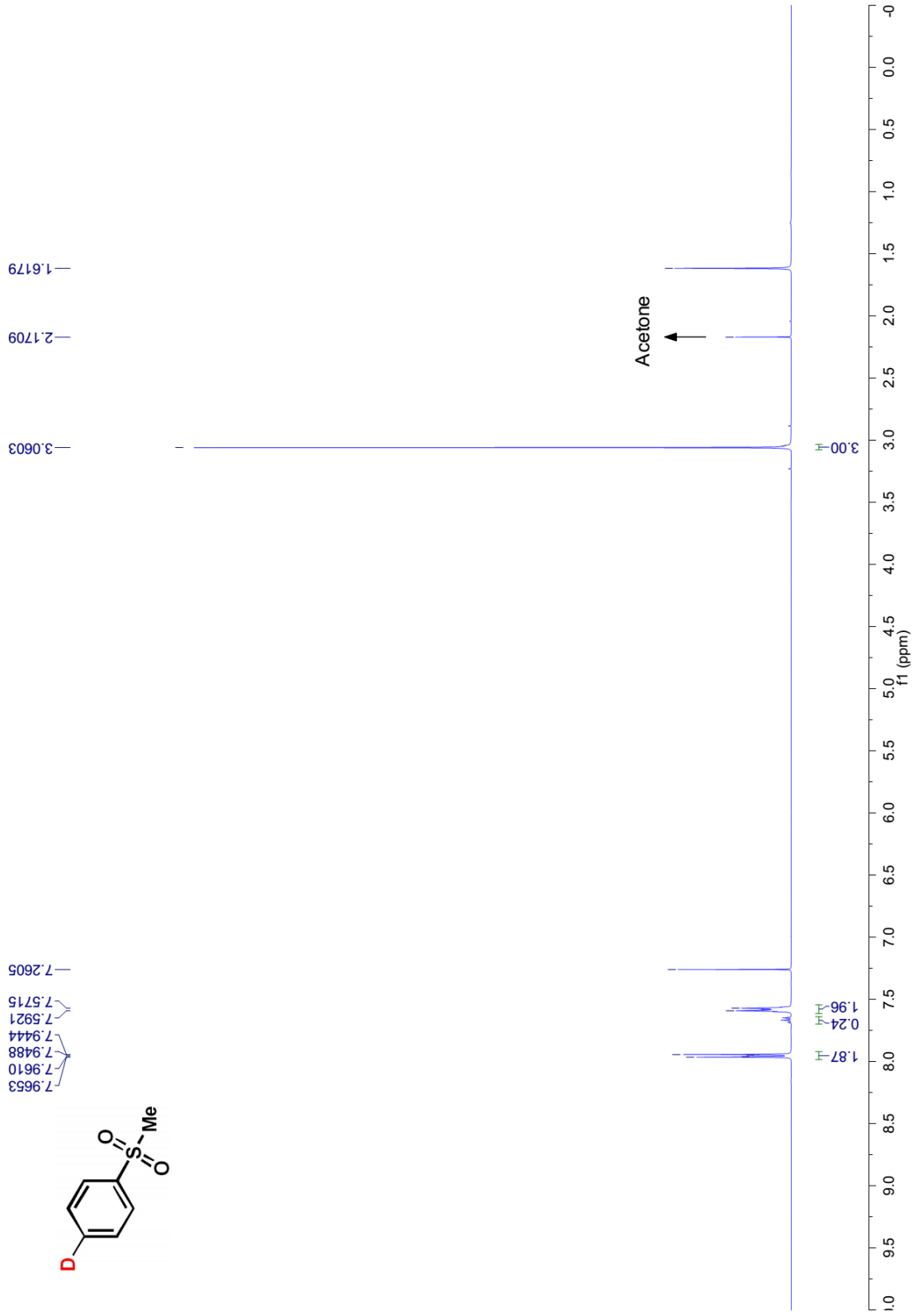

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***4j***



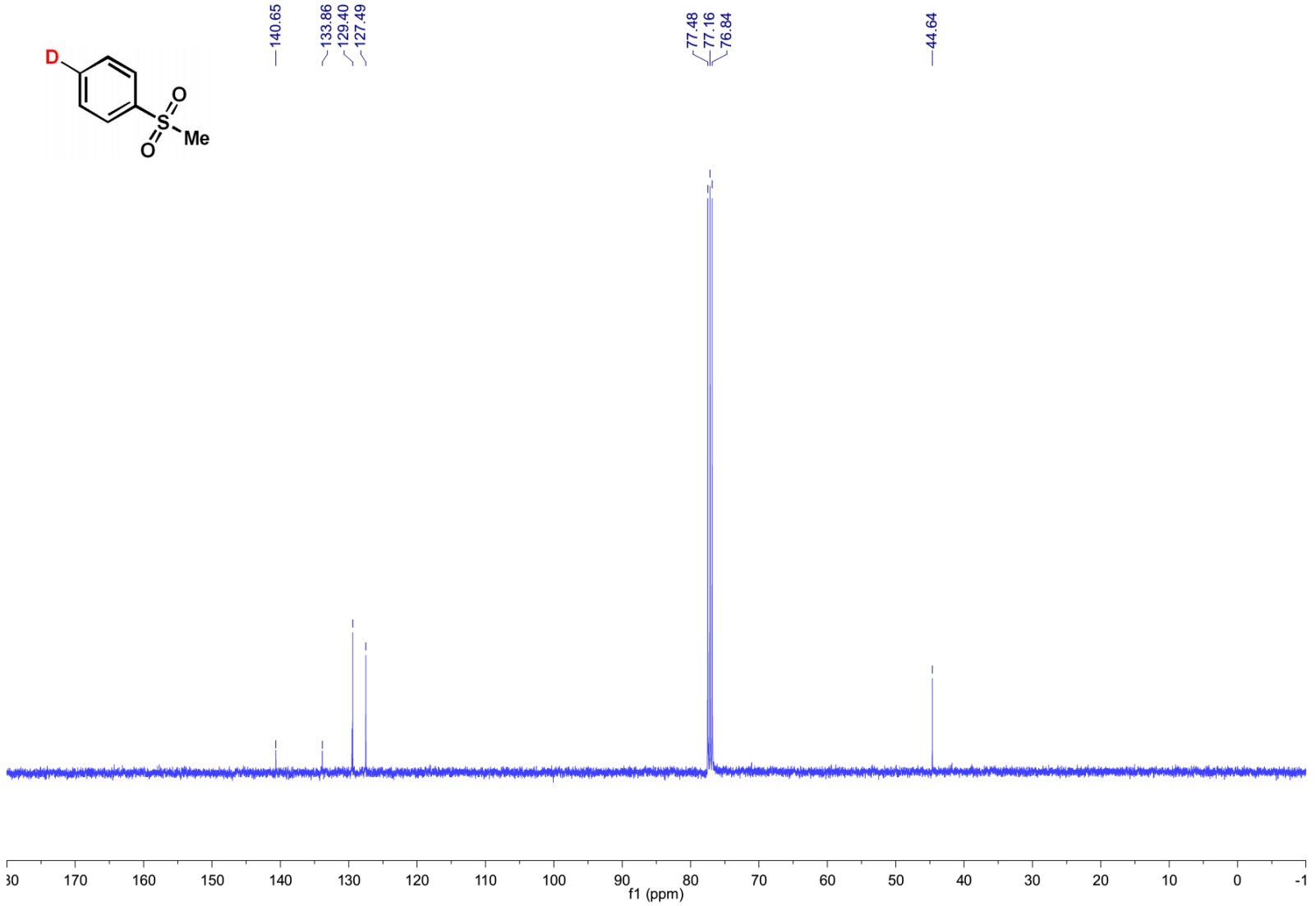

$^1$H NMR (400 MHz, $CDCl_3$) of ***4k***



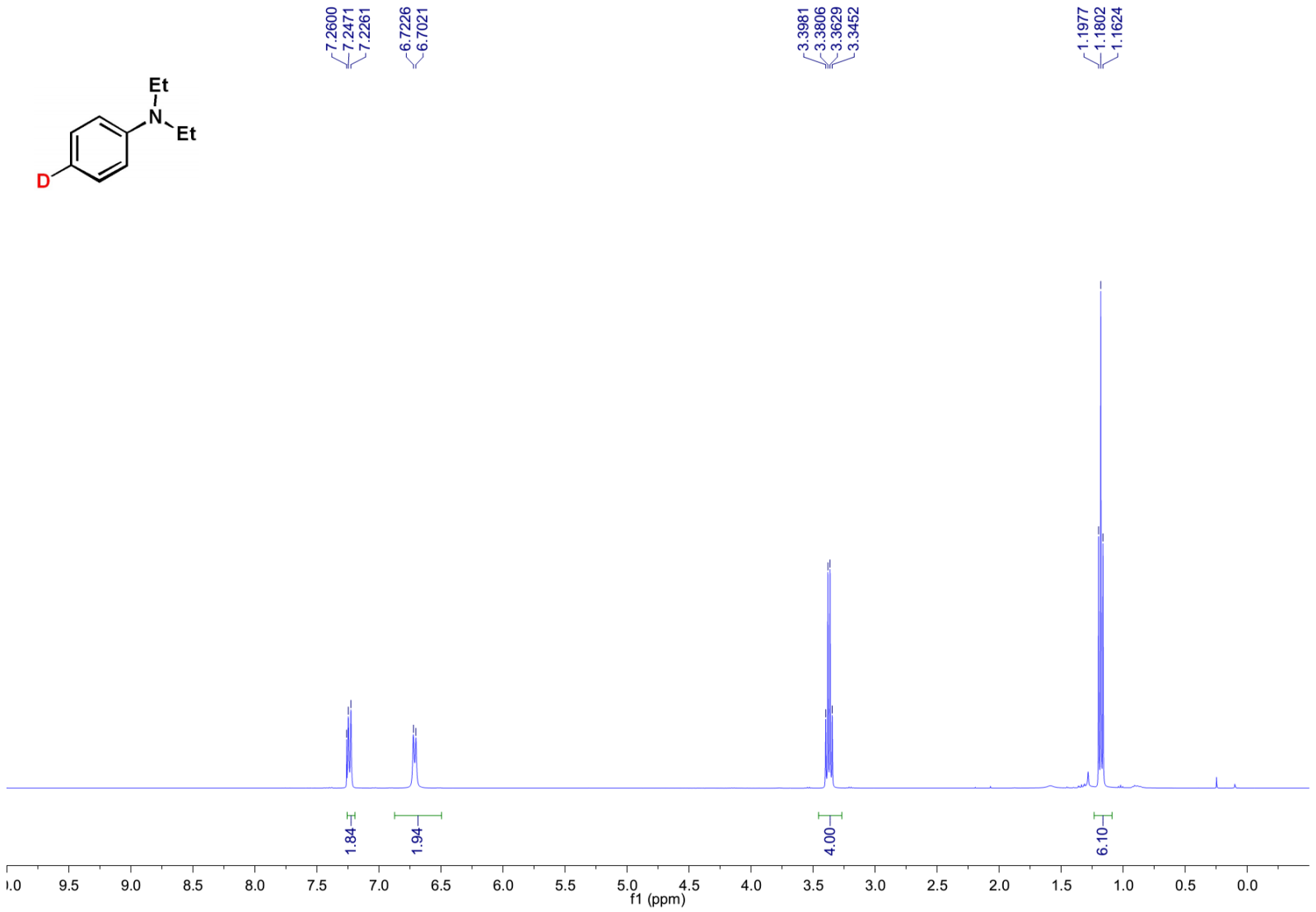

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***4k***



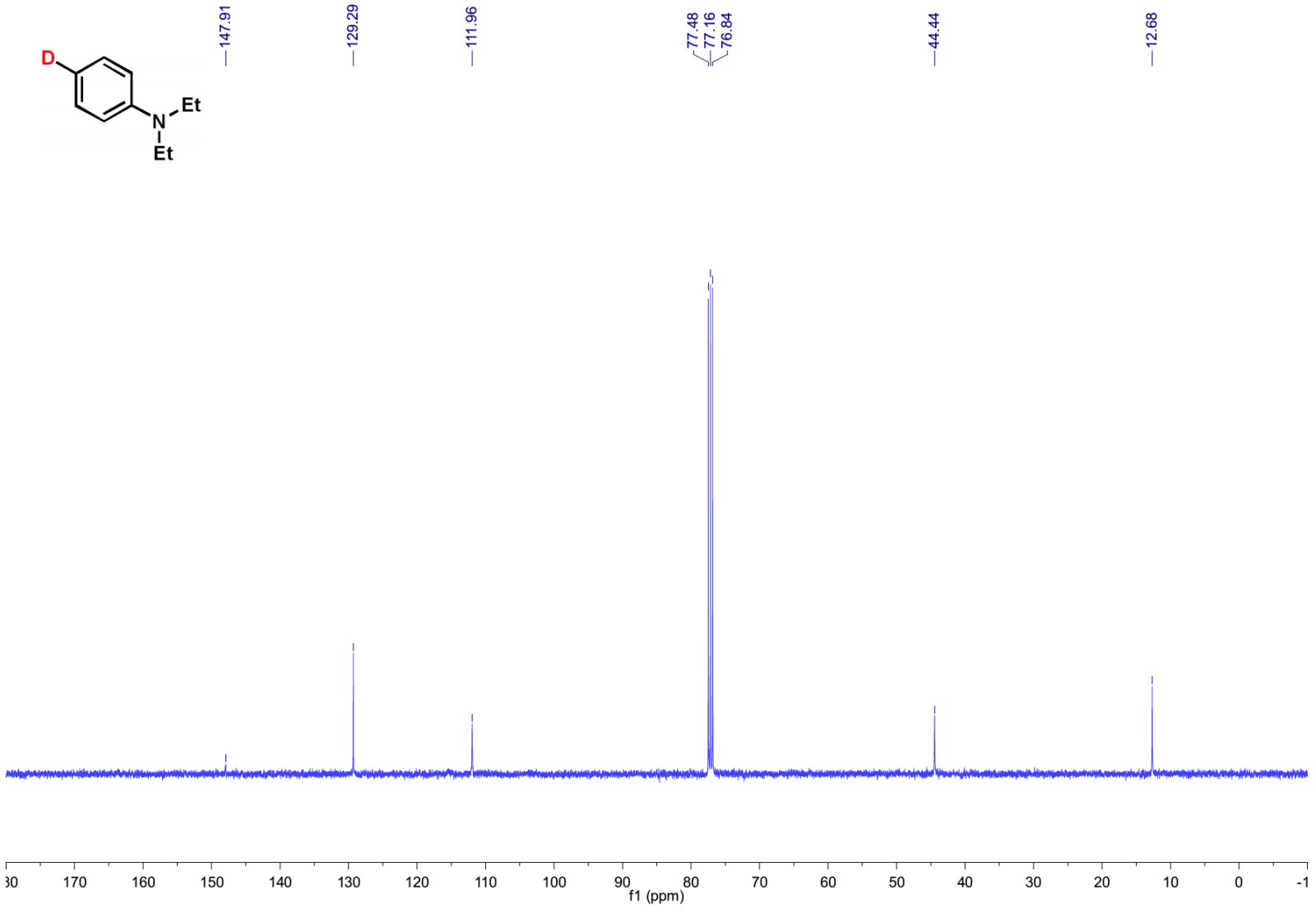

$^1$H NMR (400 MHz, $CDCl_3$) of ***4l***



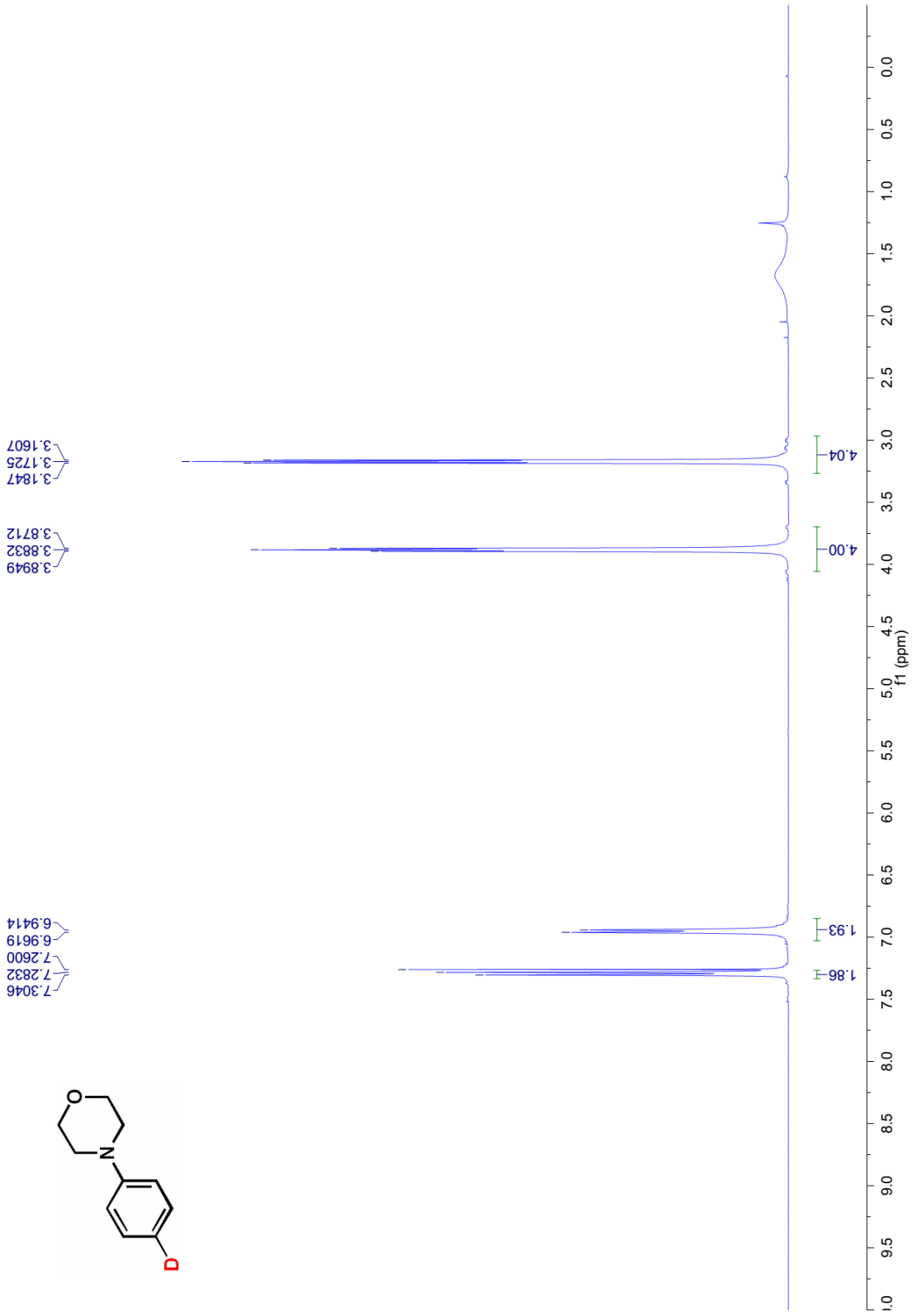

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***4l***



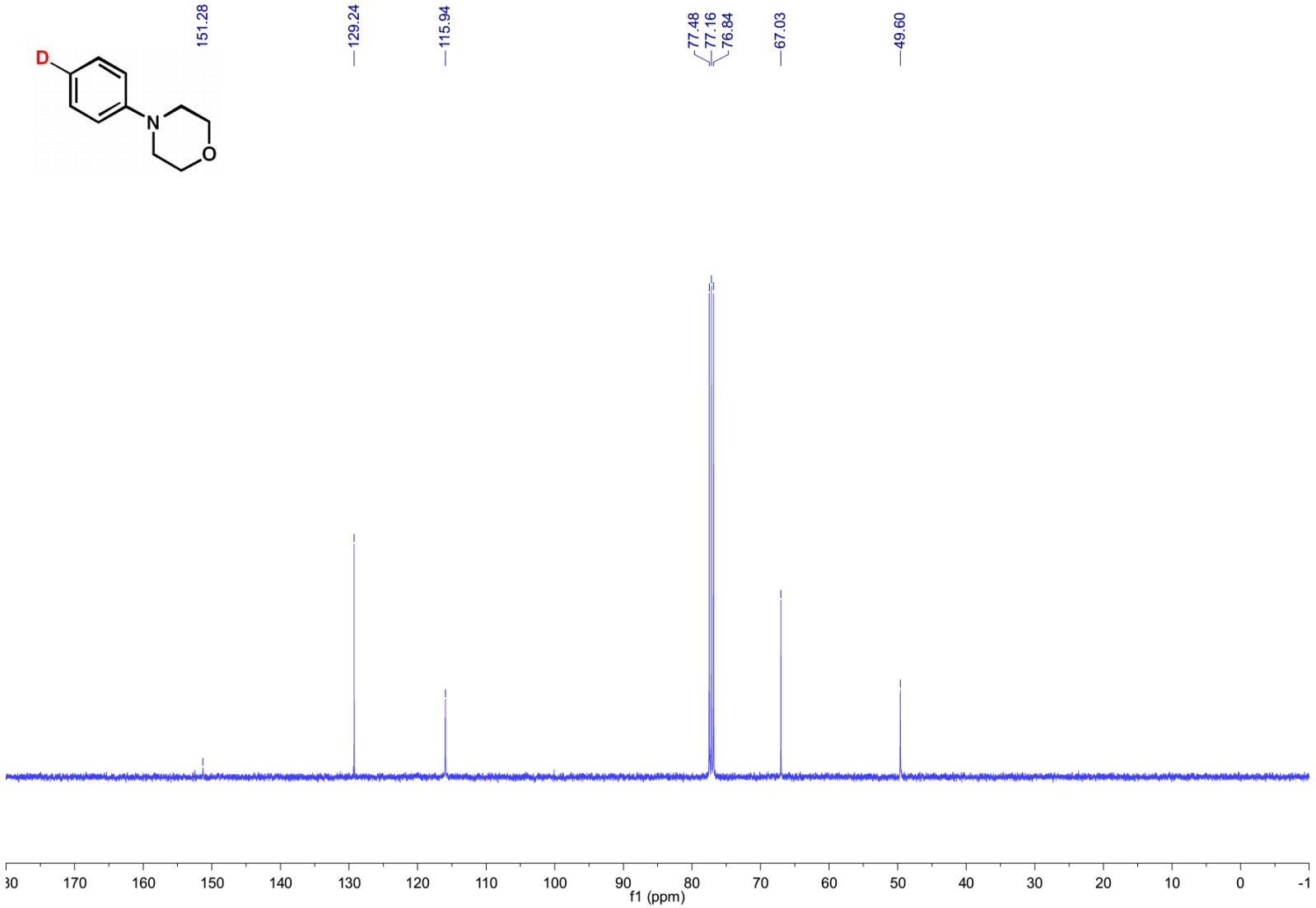

$^1$H NMR (400 MHz, $CDCl_3$) of ***4m***



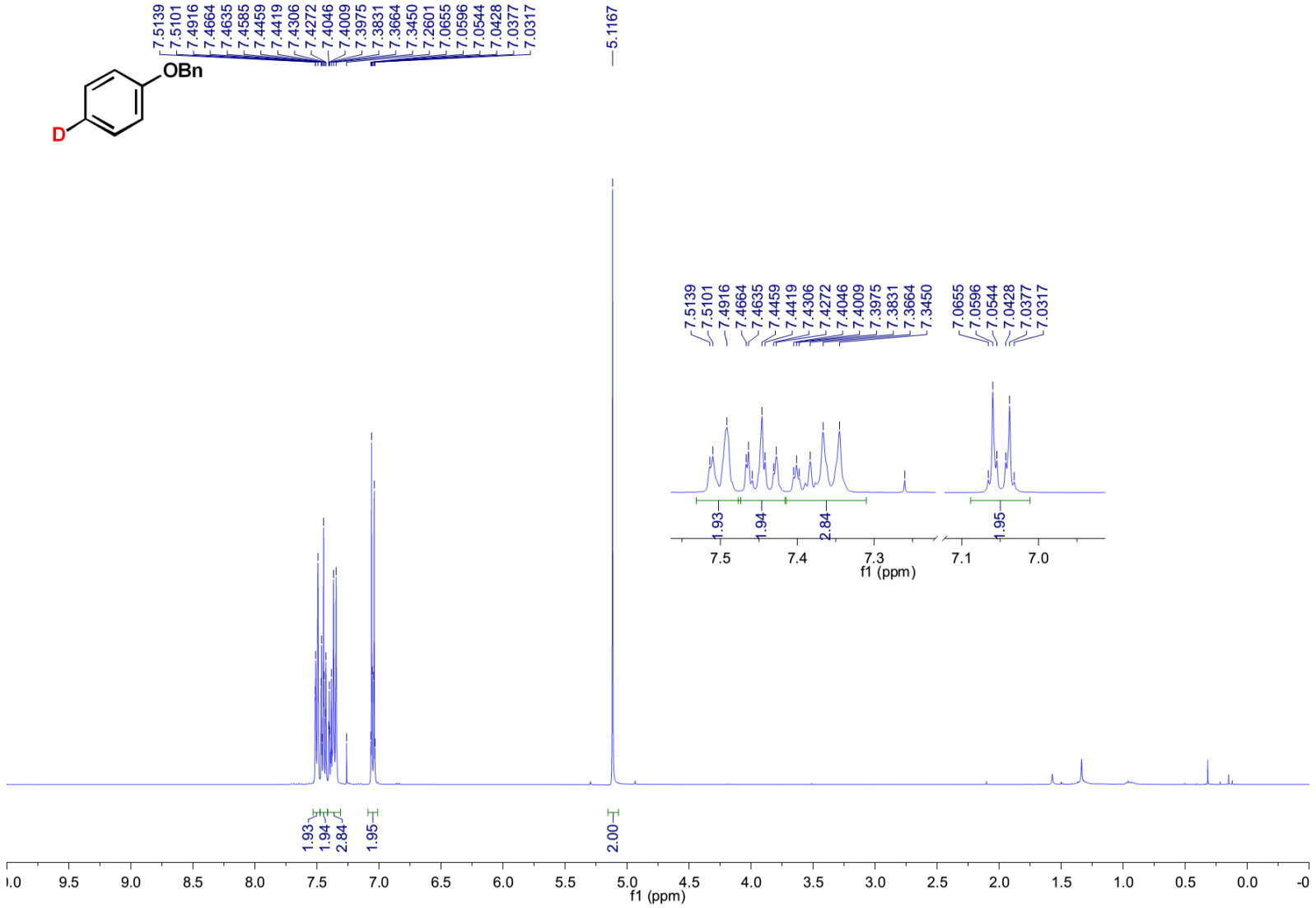

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***4m***



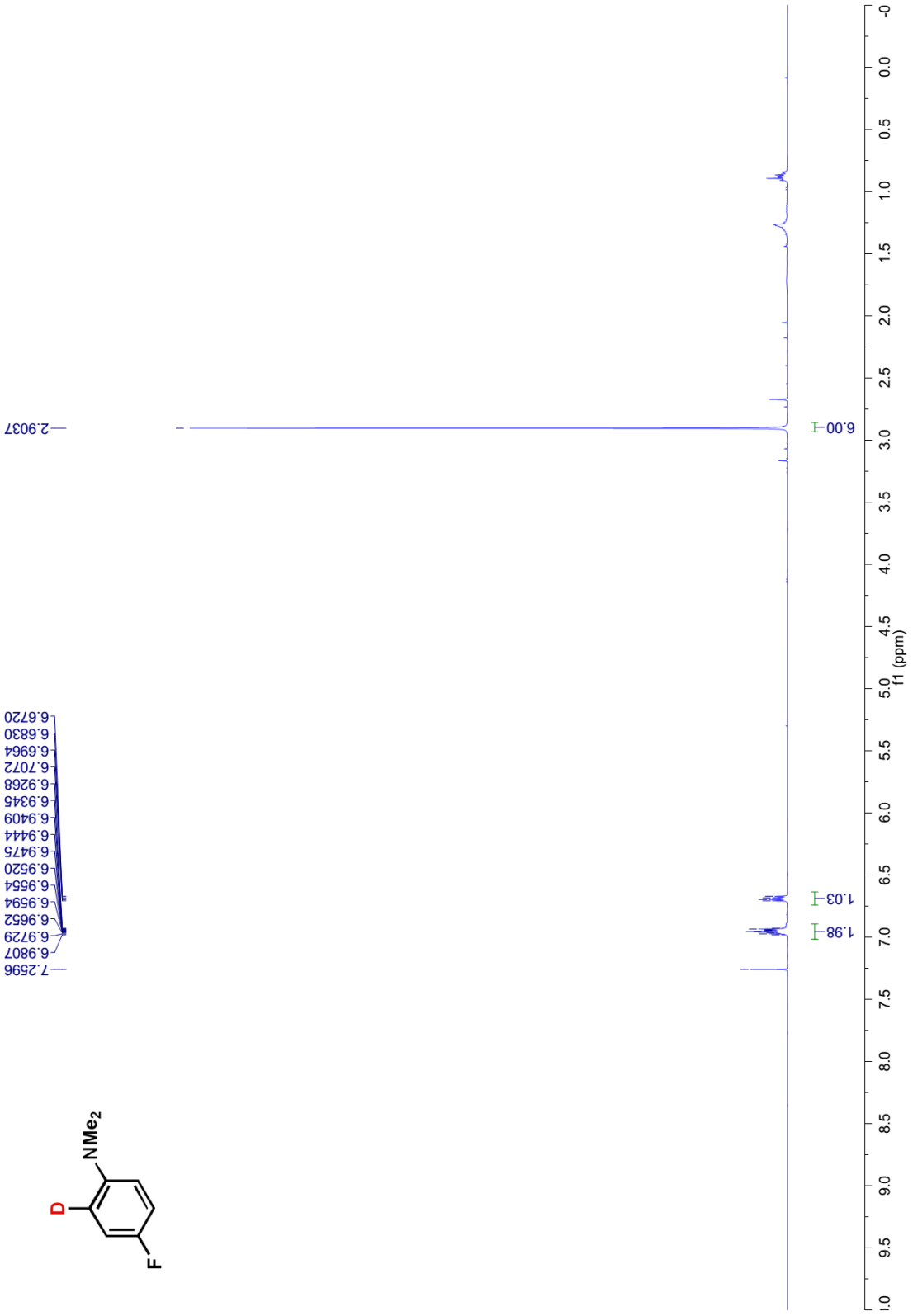

$^1$H NMR (400 MHz, $CDCl_3$) of ***4n***



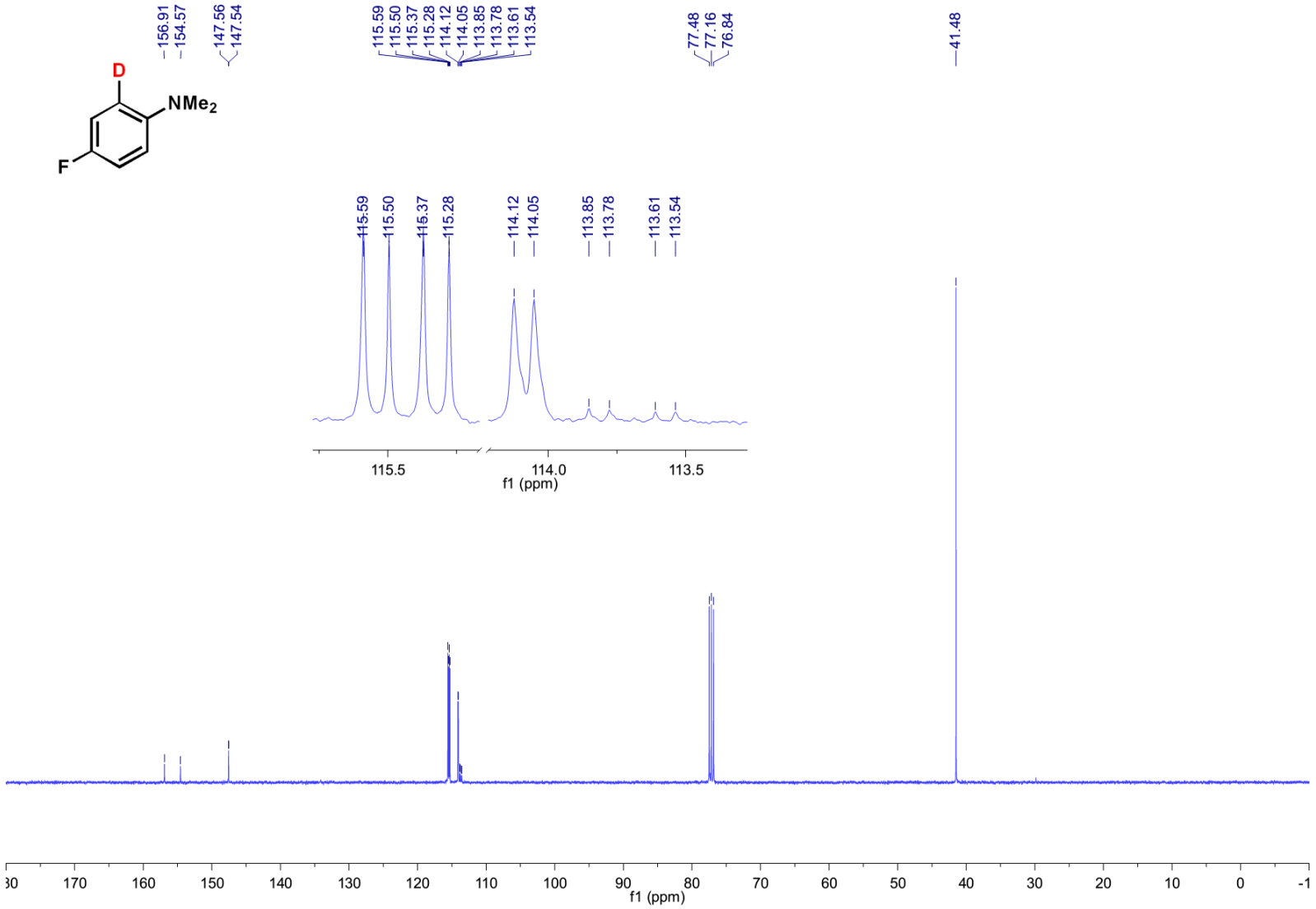

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***4n***



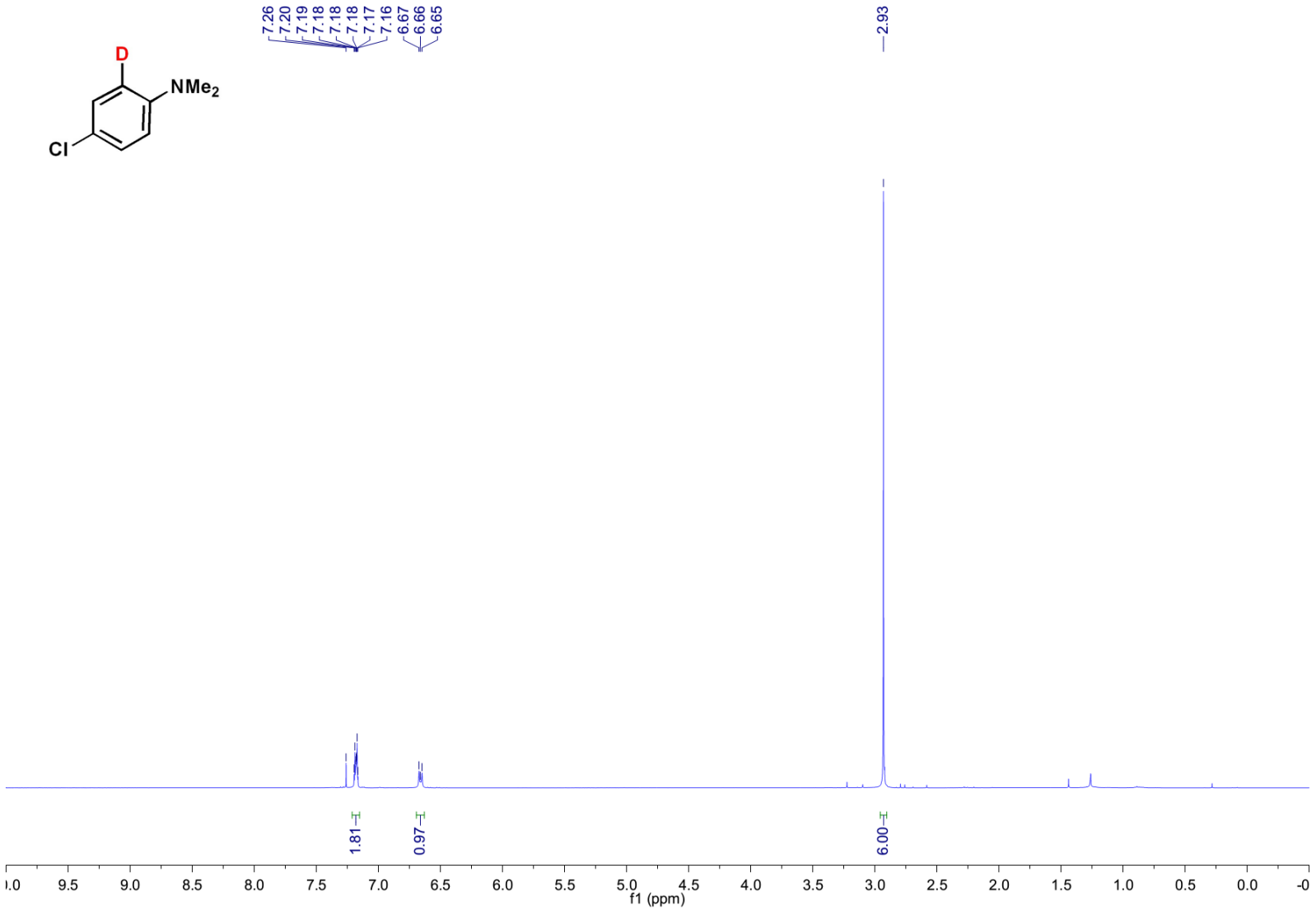

$^{1}$H NMR (400 MHz, $CDCl_3$) of ***4o***



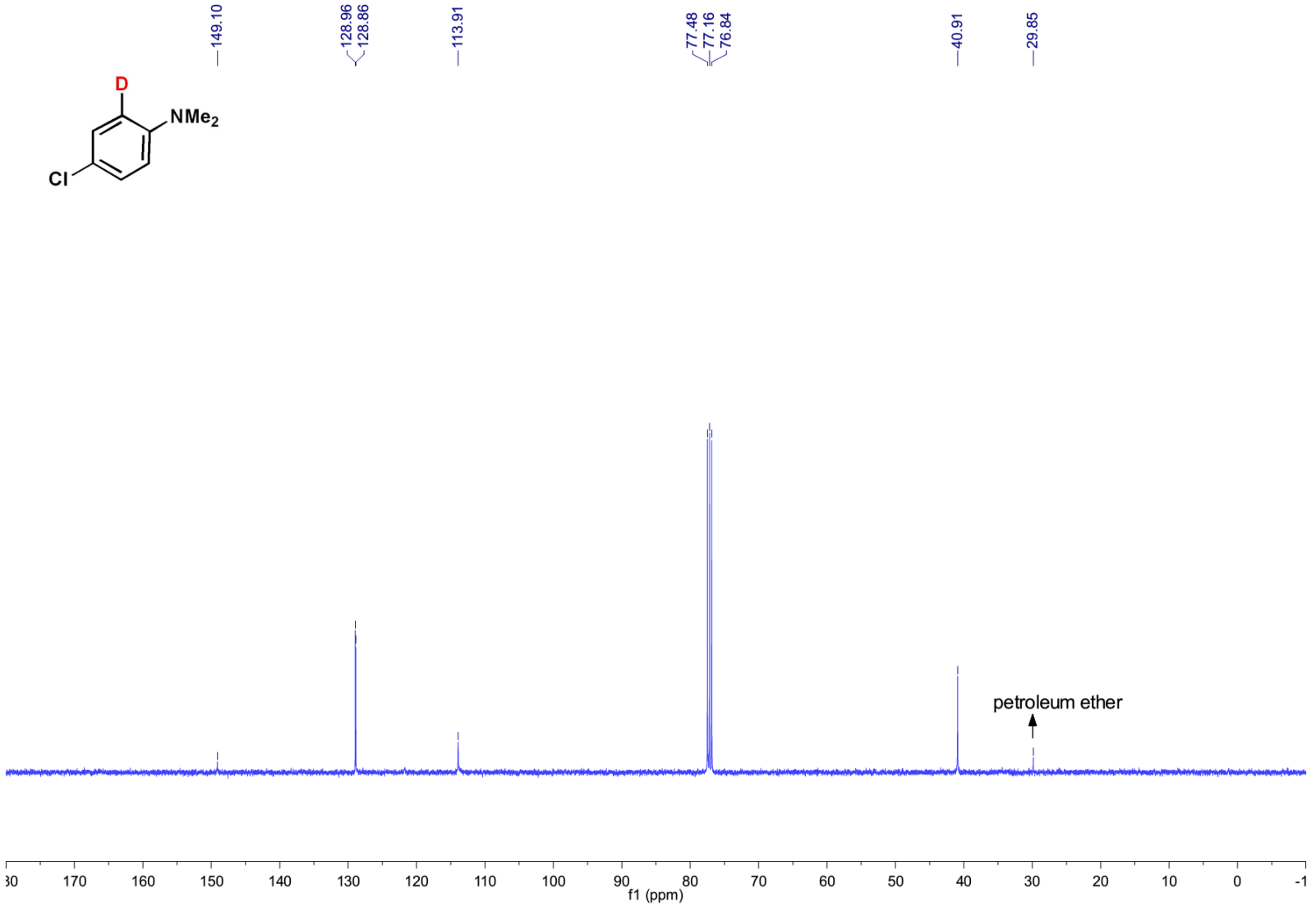

$^1$H NMR (400 MHz, $CDCl_3$) of ***4p***



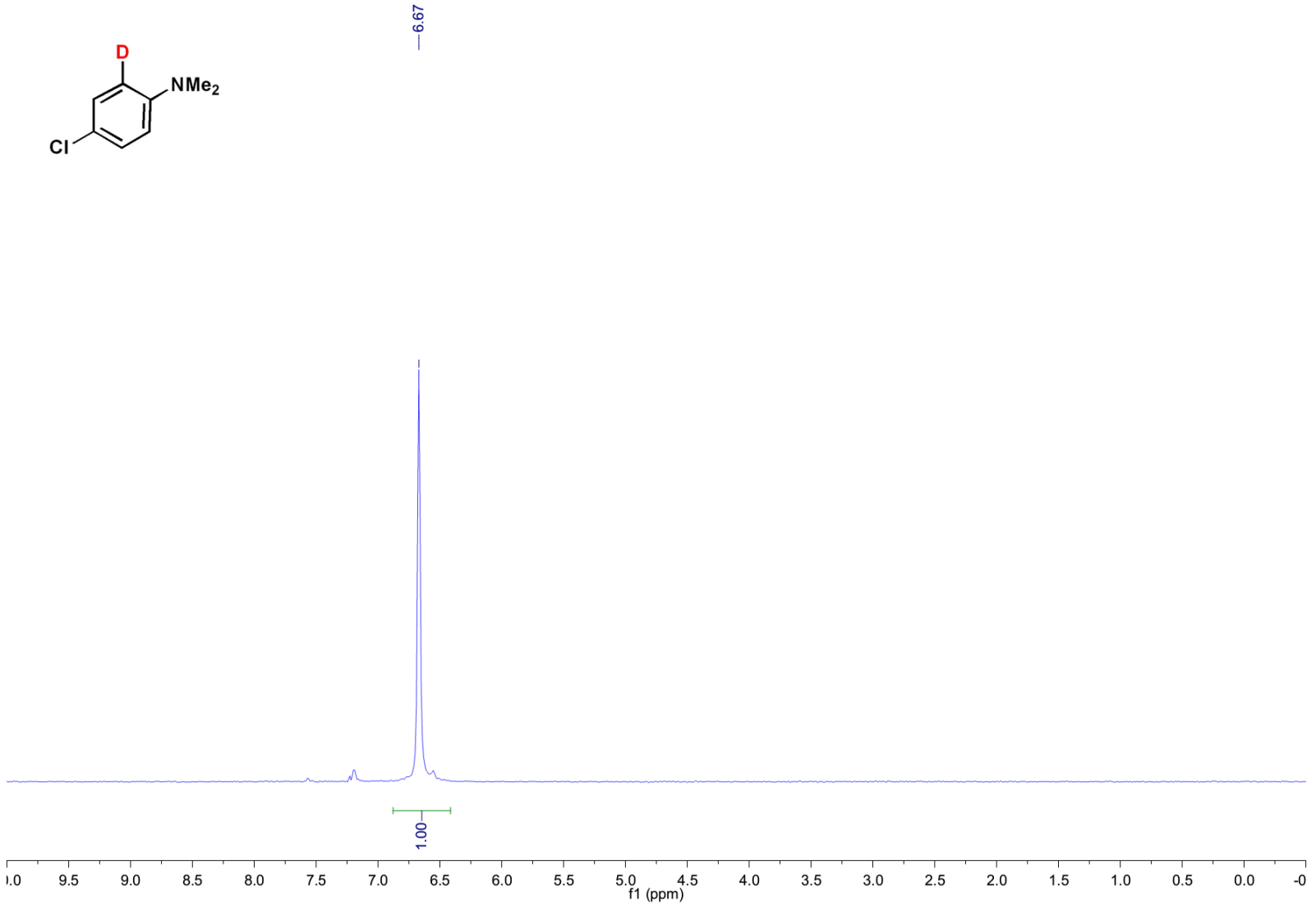

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***4p***



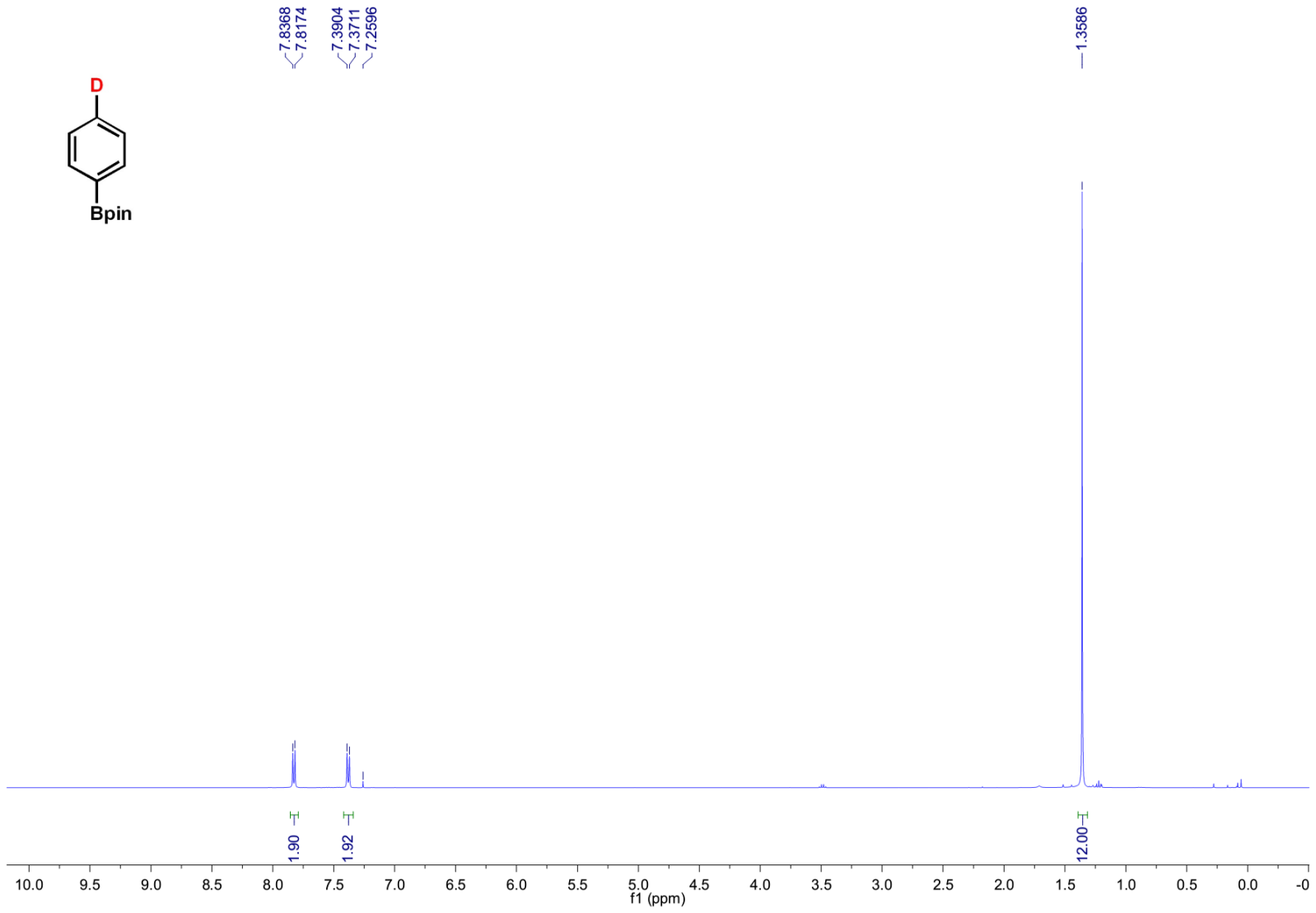

$^{1}$H NMR (400 MHz, $CDCl_3$) of ***4q***



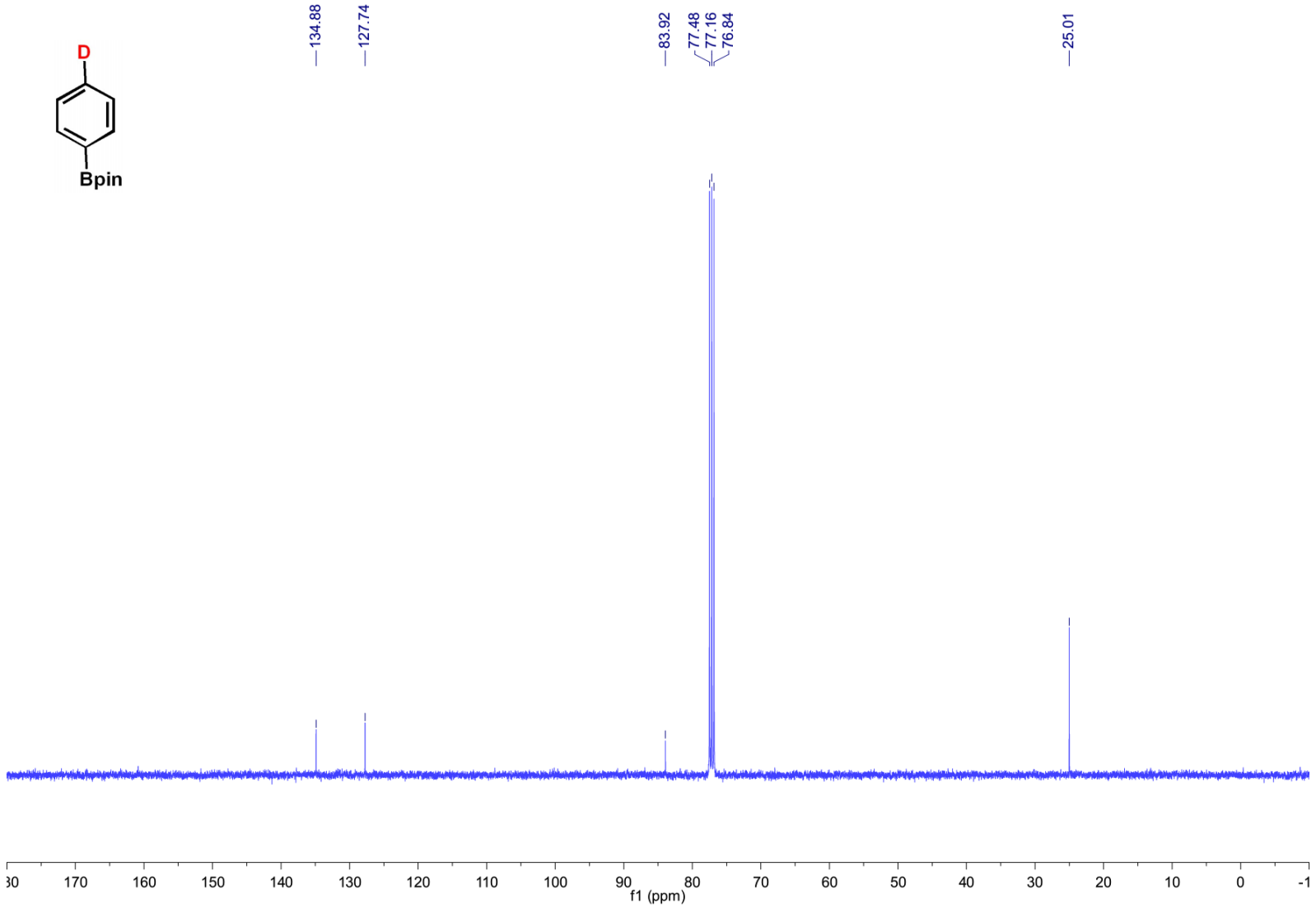

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***4q***



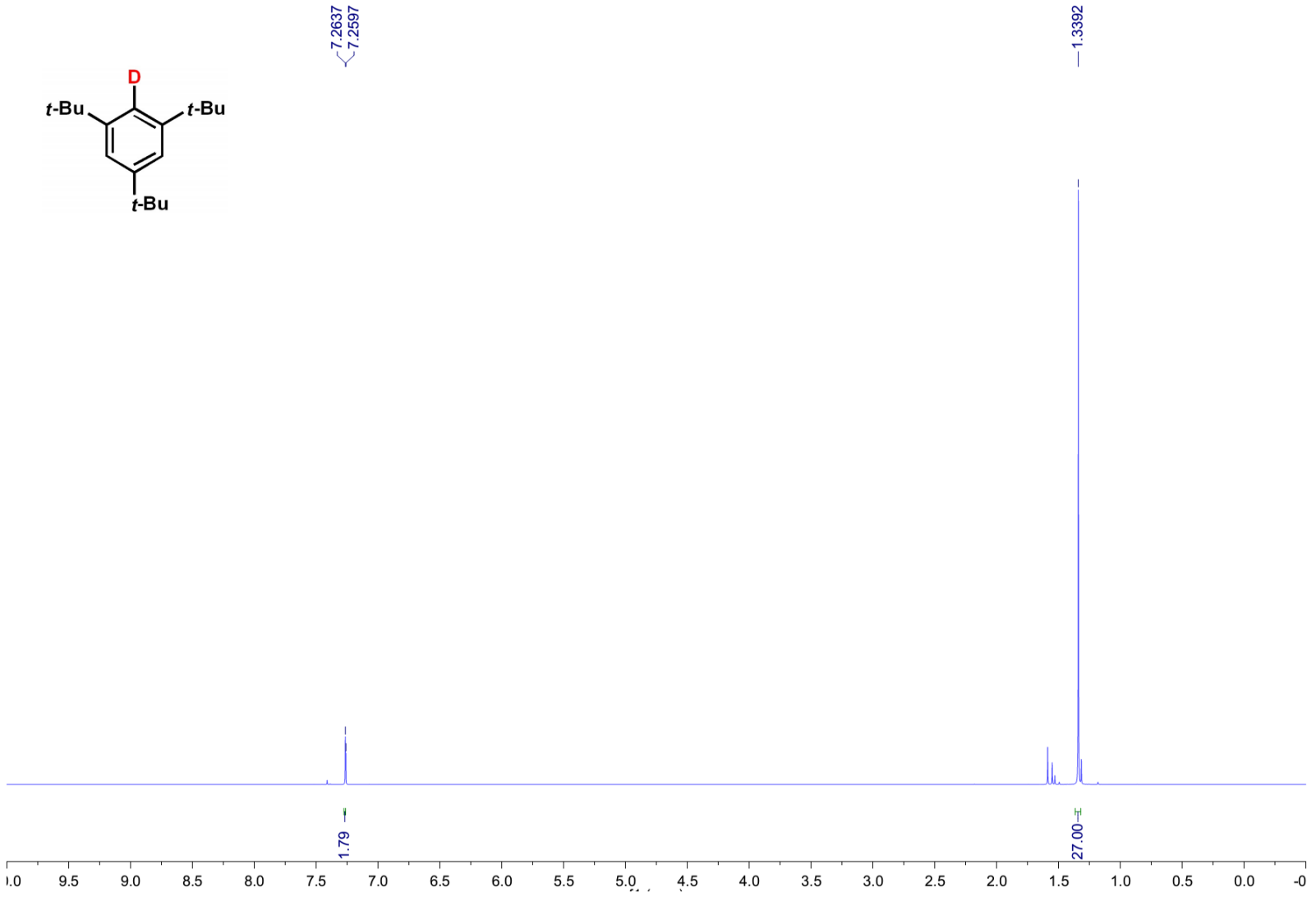

$^{2}$H NMR (122 MHz, $CHCl_3$) of ***4q***



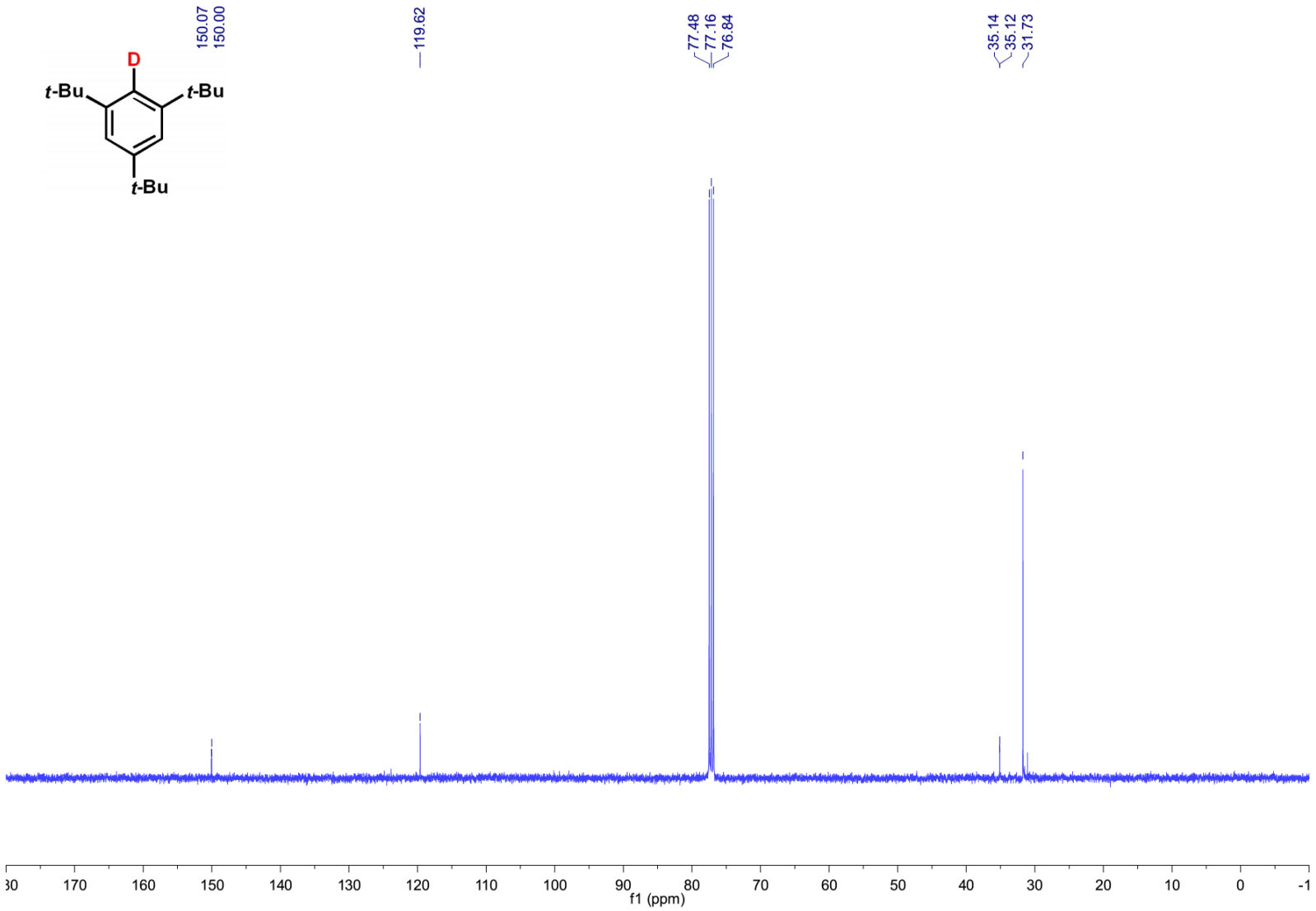

$^1$H NMR (400 MHz, $CDCl_3$) of ***4r***




$^{13}$C NMR (100 MHz, $CDCl_3$) of ***4r***




$^1$H NMR (400 MHz, $CDCl_3$) of ***4s***

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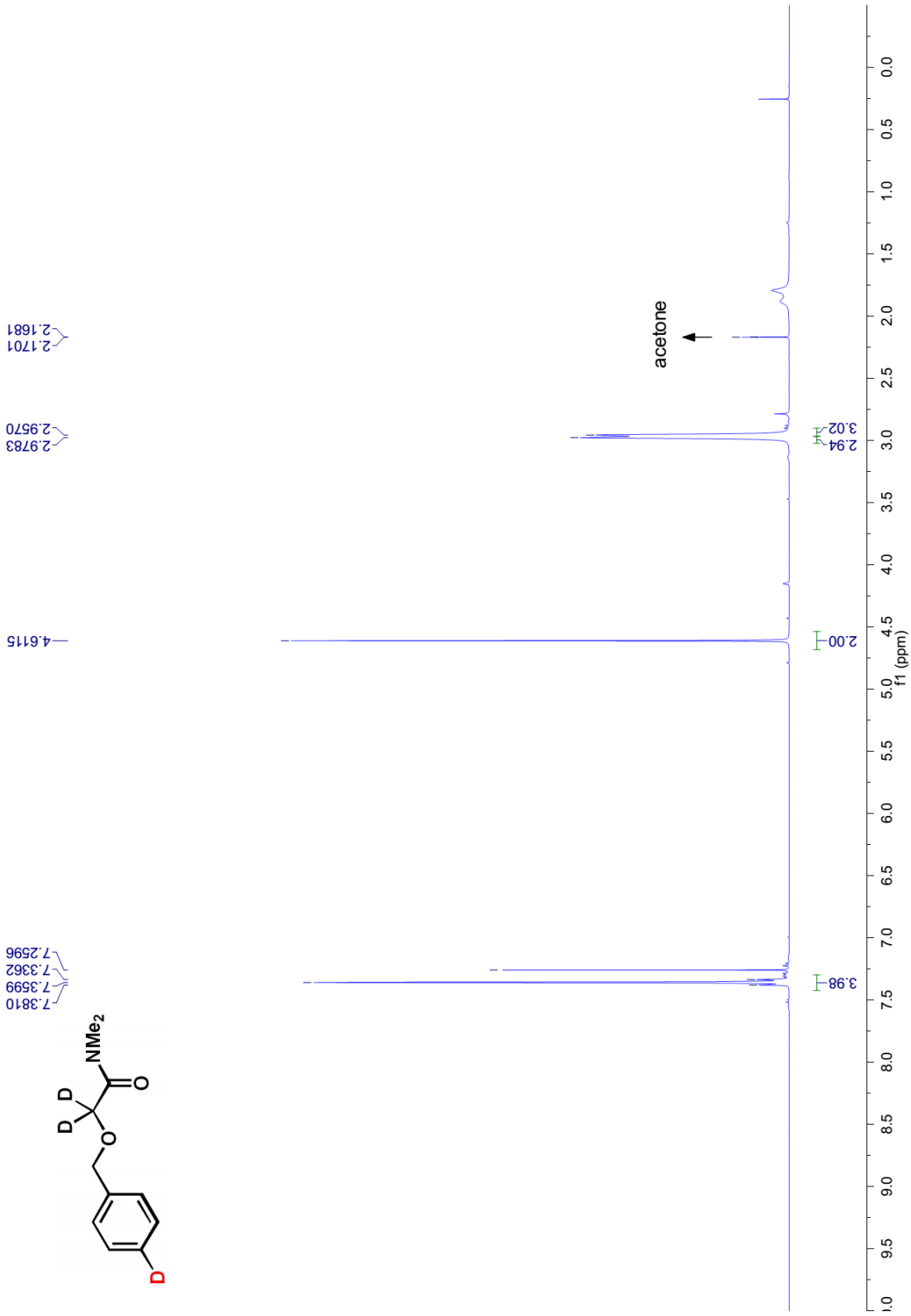
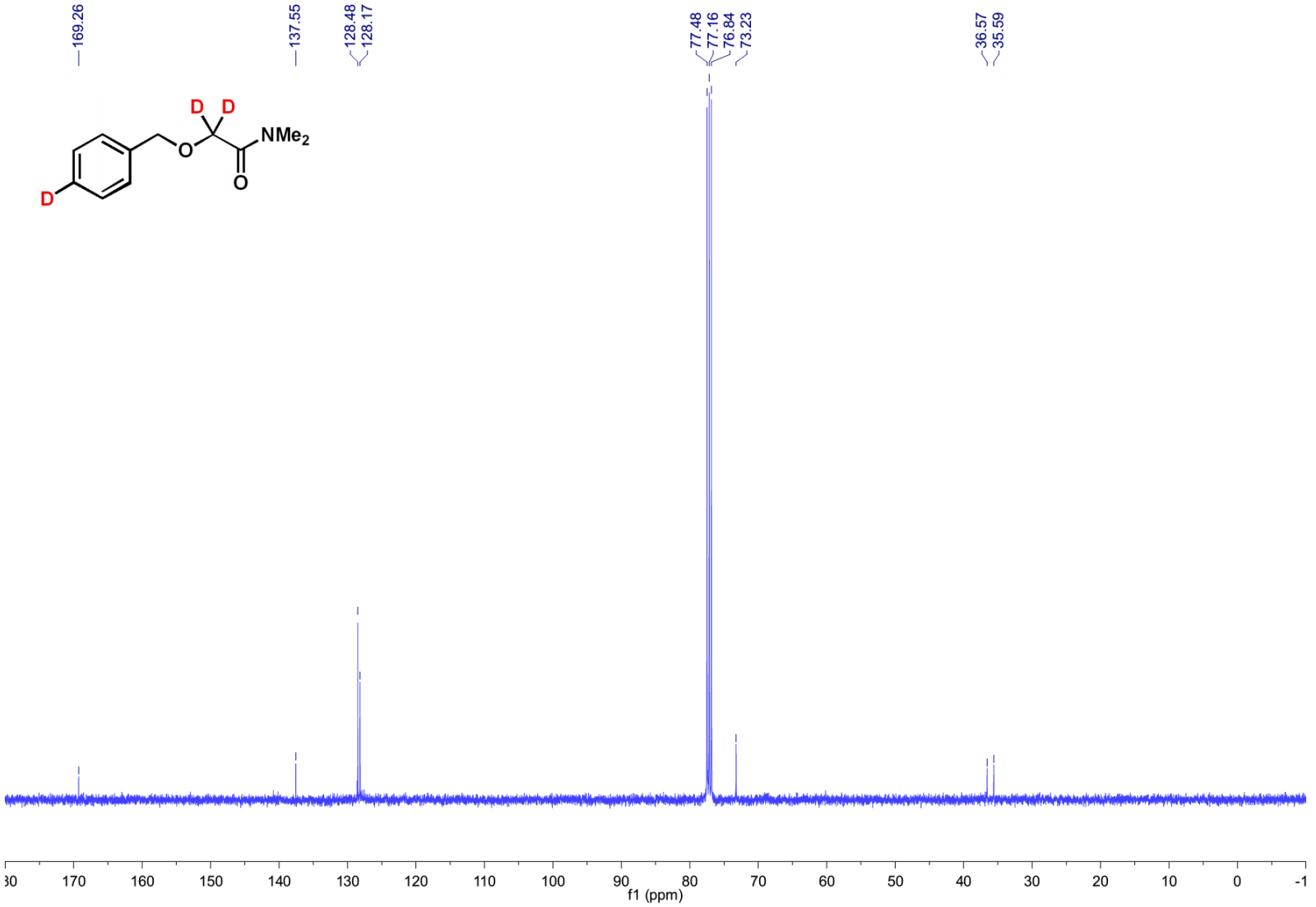
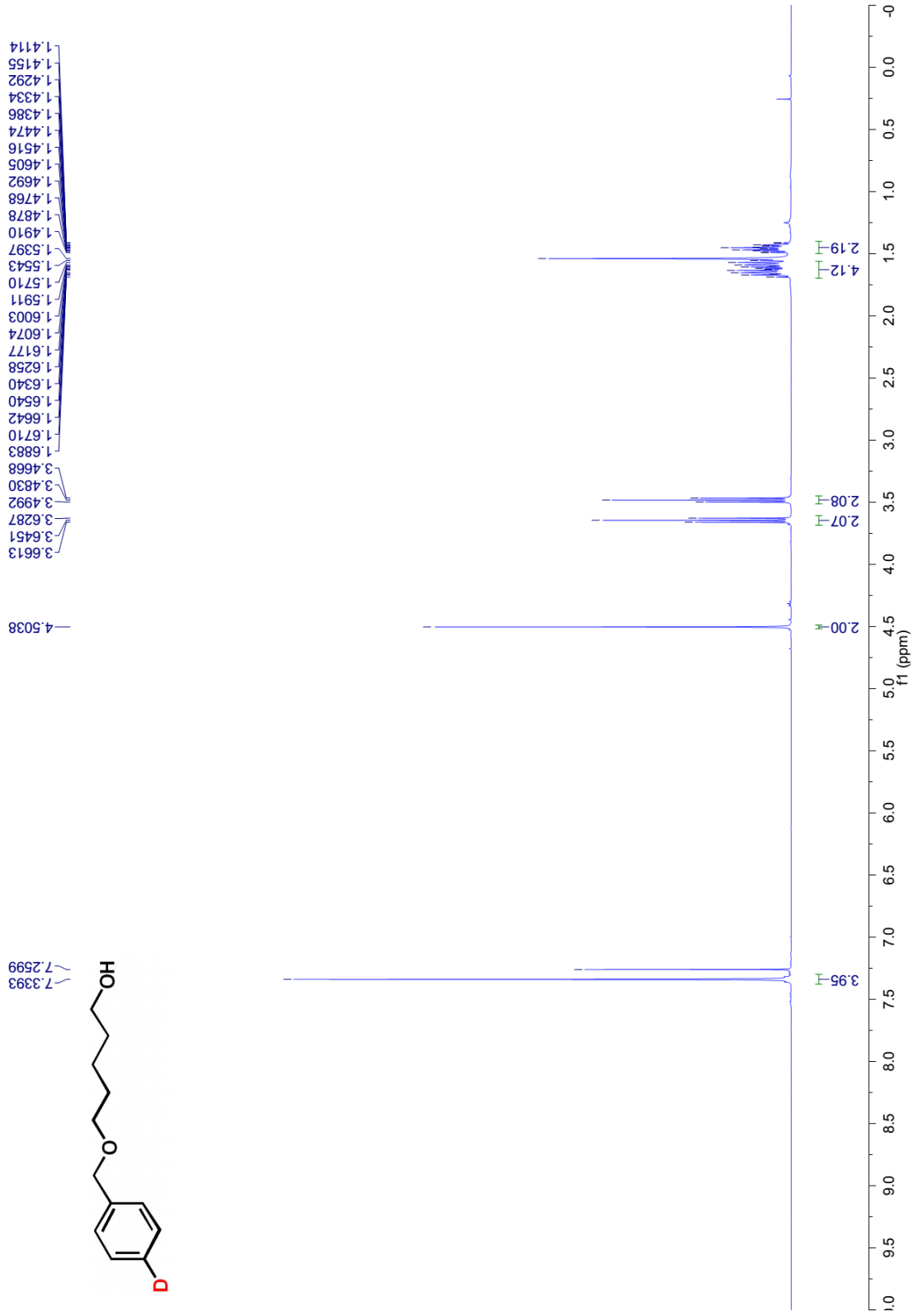


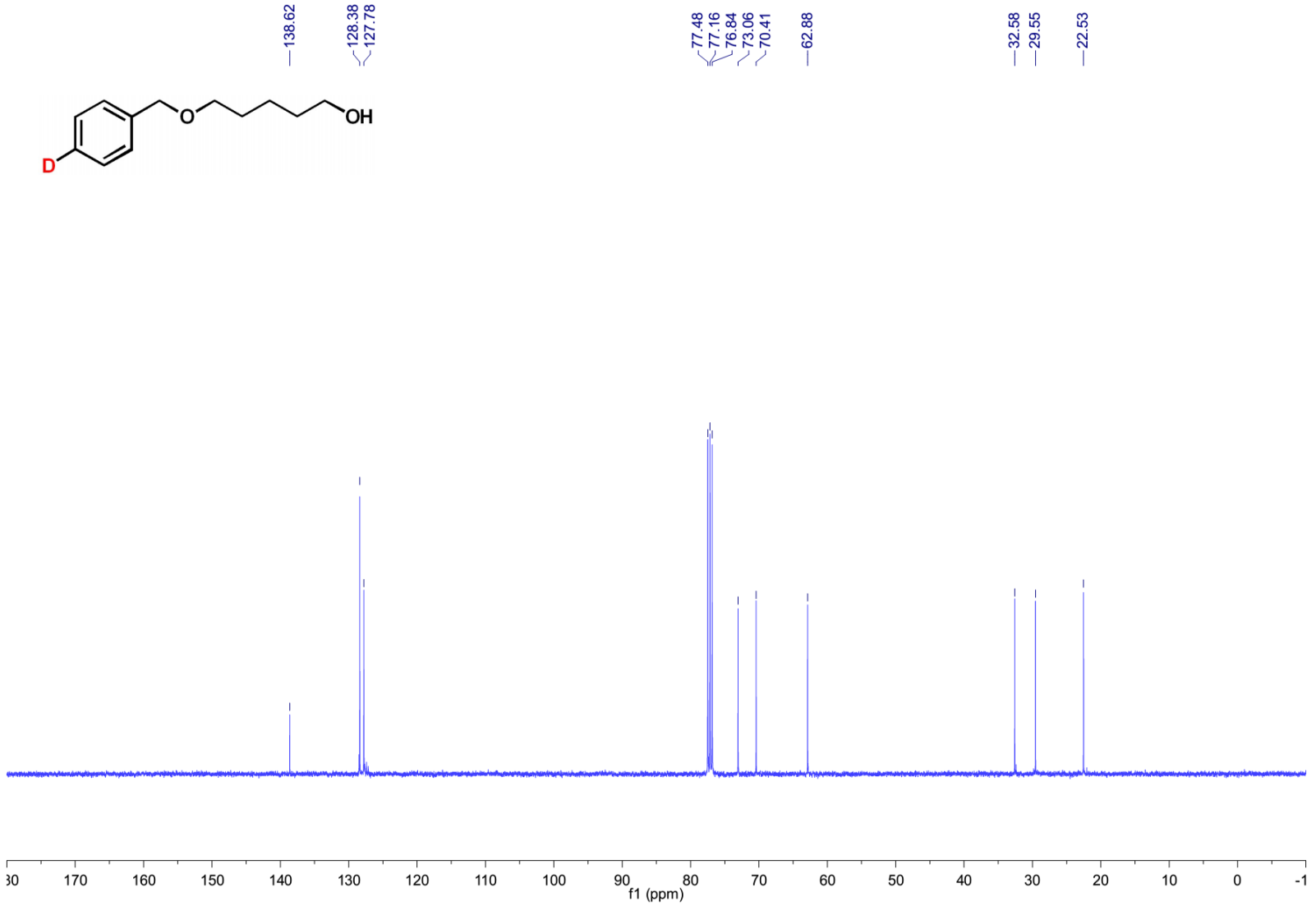

$^1$H NMR (400 MHz, $CDCl_3$) of ***5a***



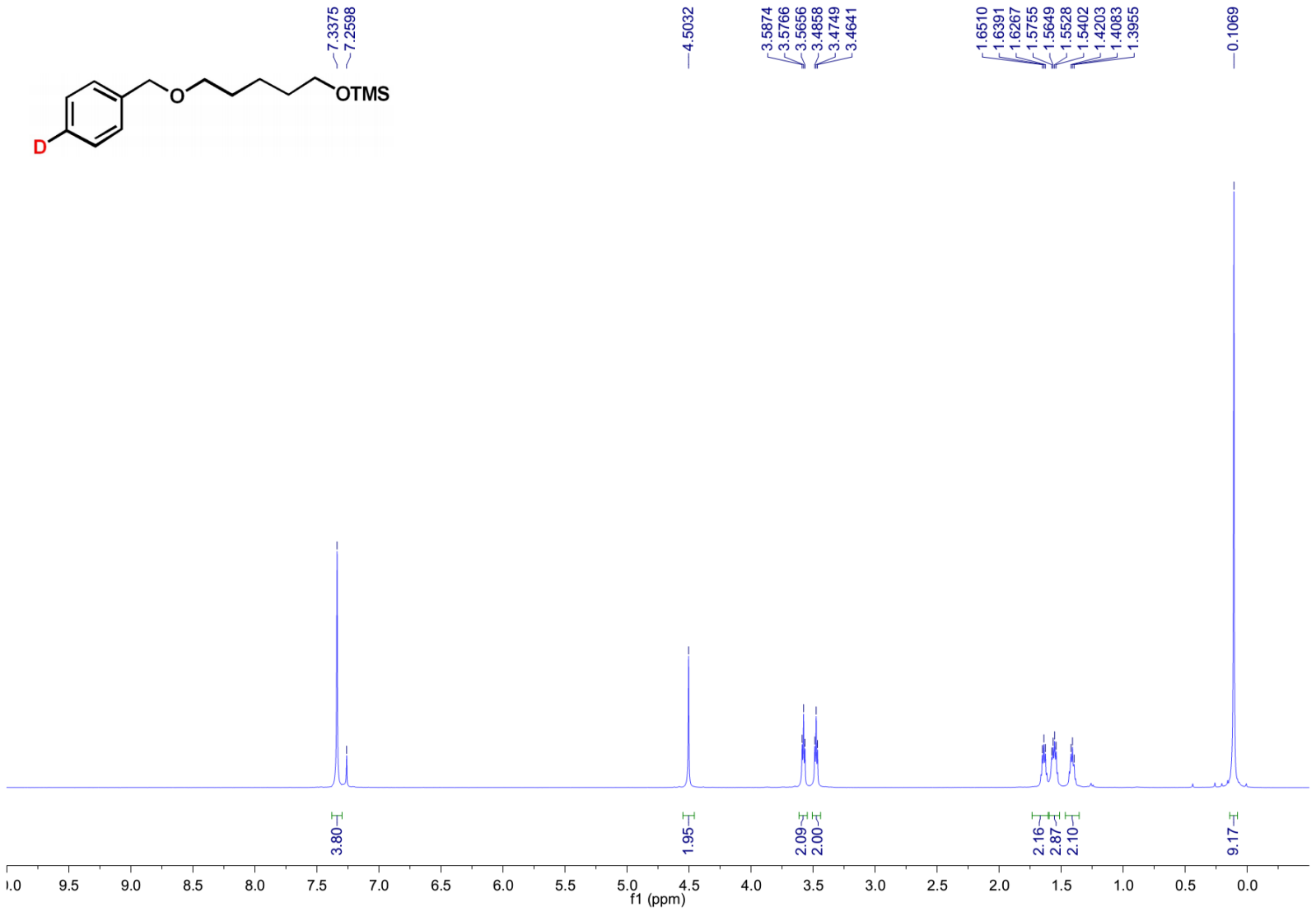

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***5a***



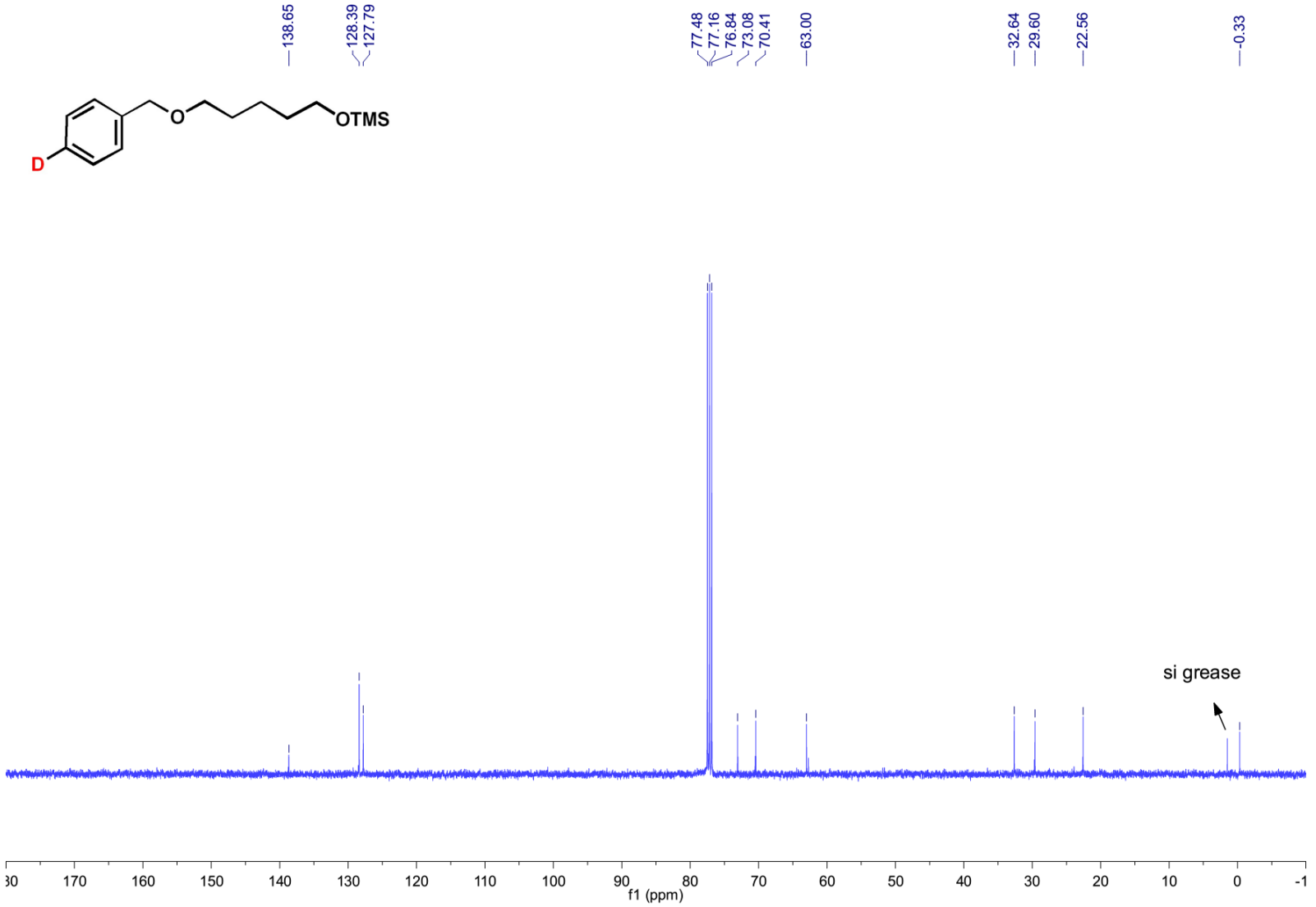

$^1$H NMR (400 MHz, $CDCl_3$) of ***5b***



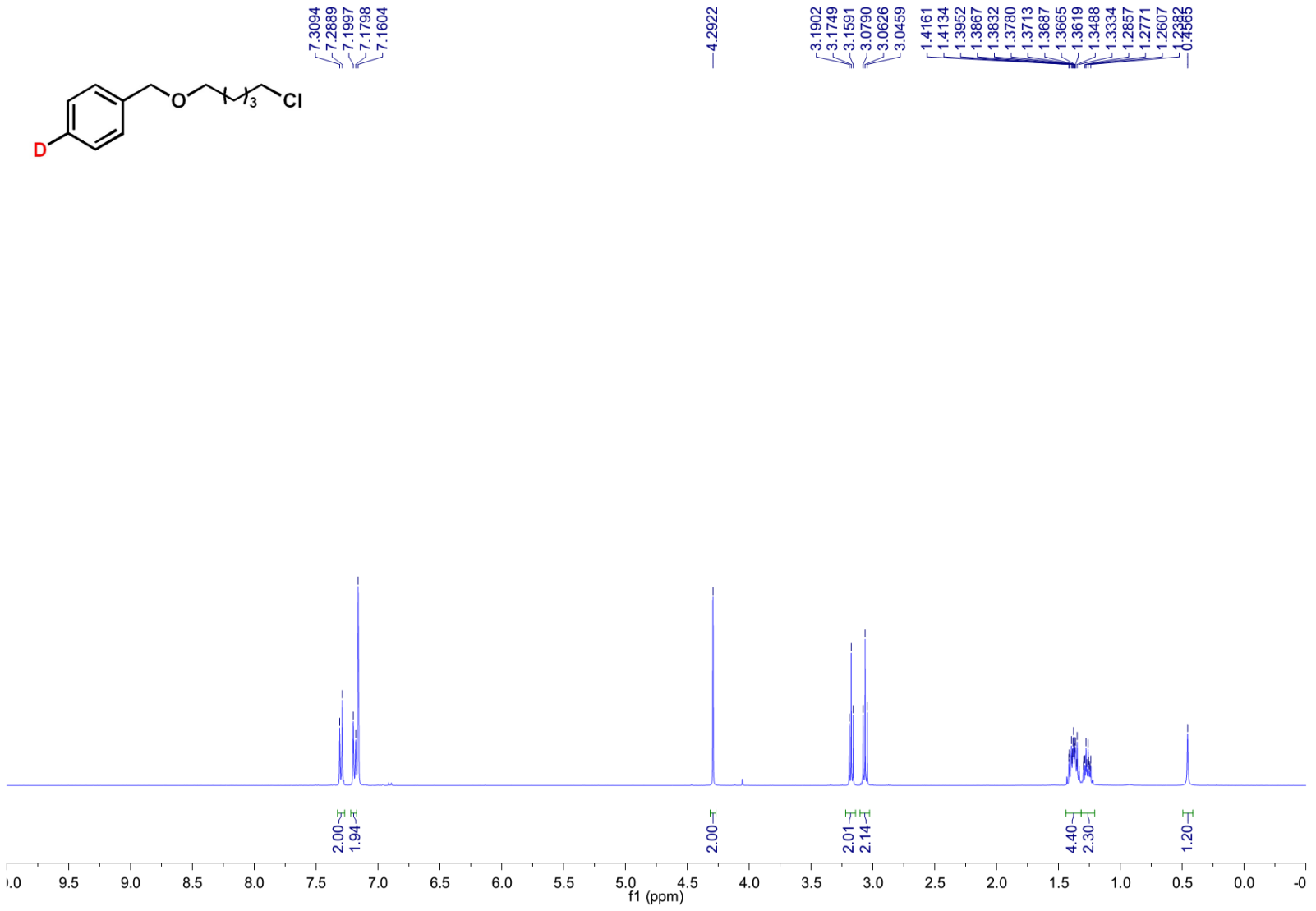

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***5b***



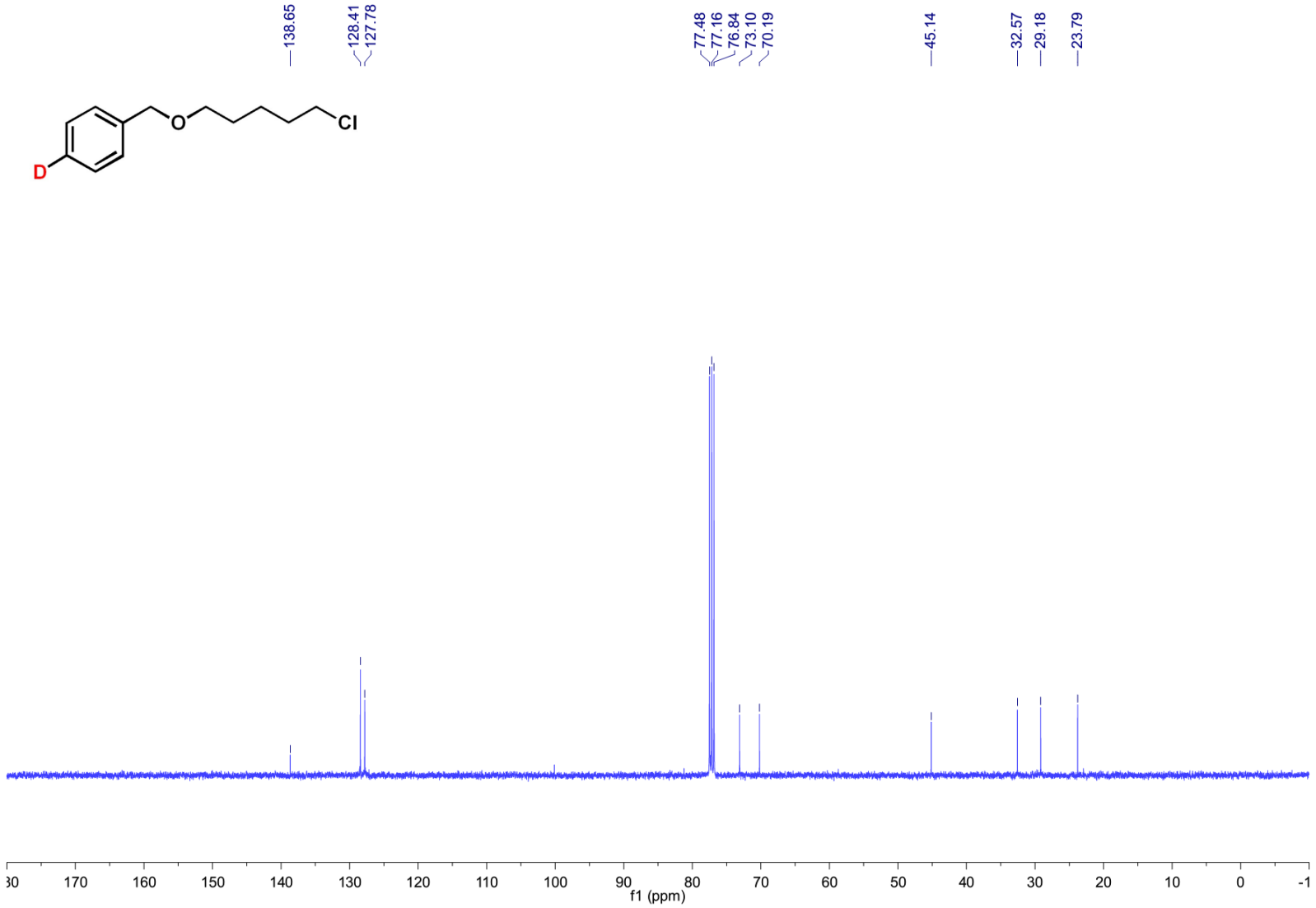

$^{1}$H NMR (400 MHz, $CDCl_3$) of ***5b'***



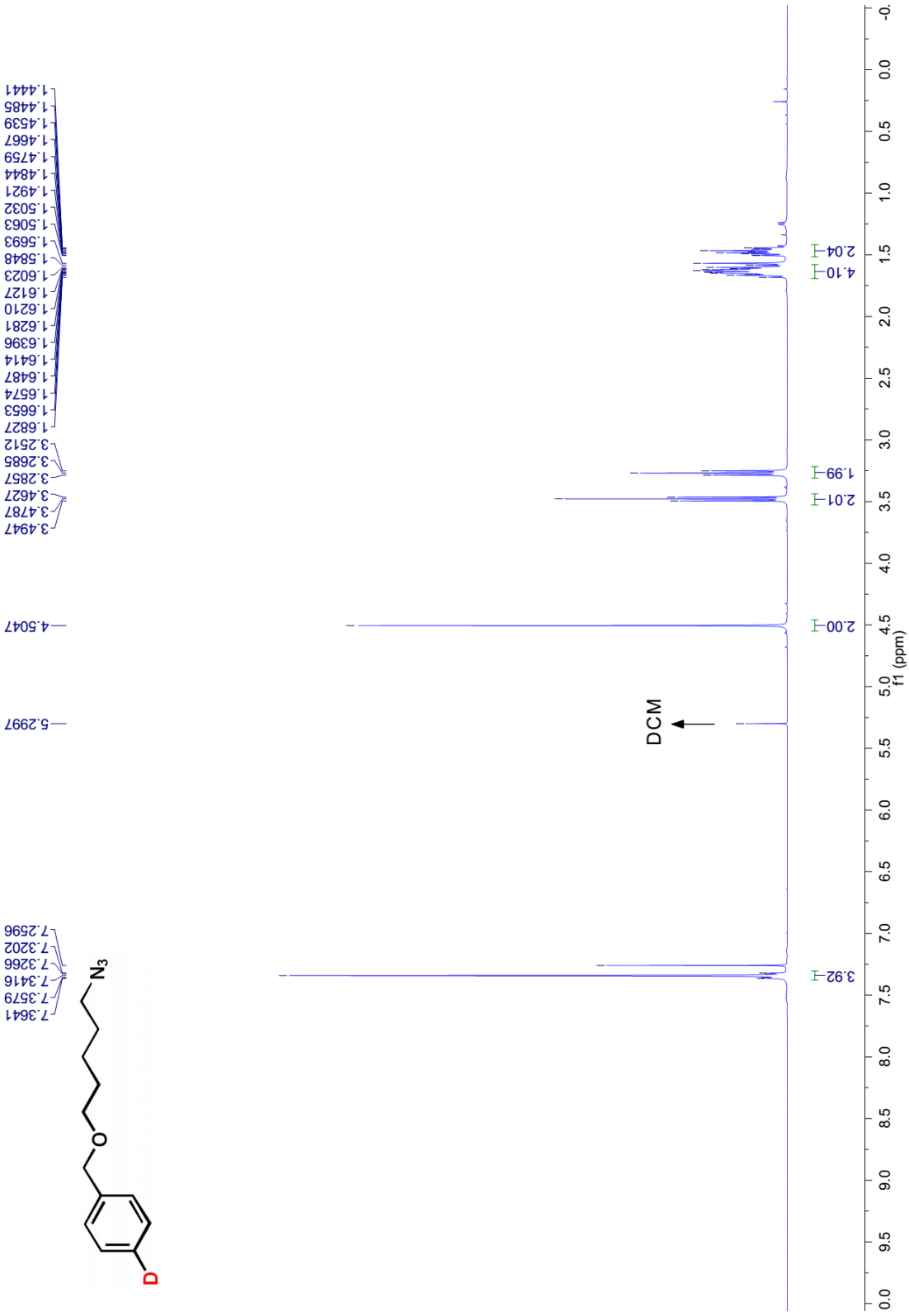

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***5b'***



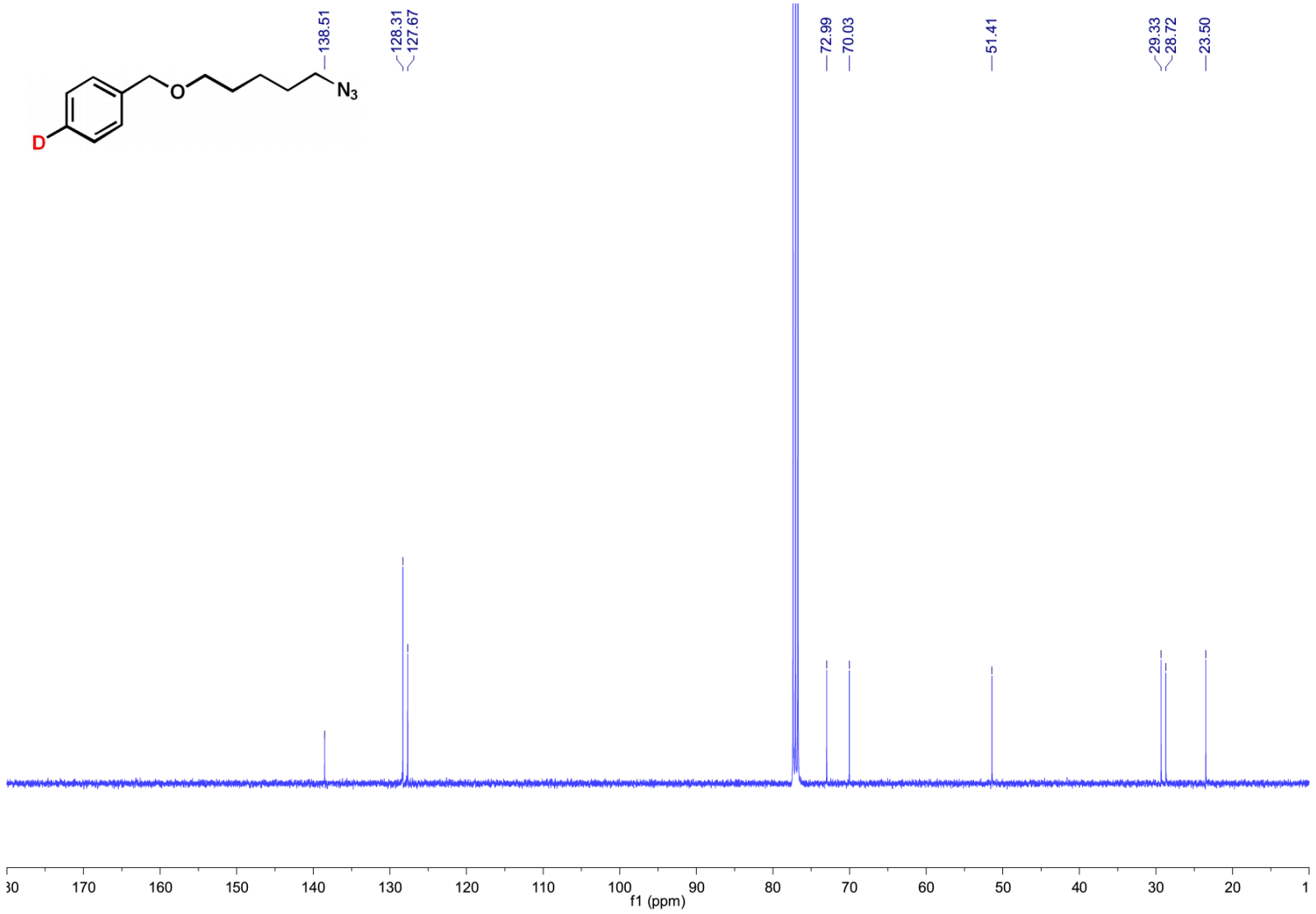

$^1$H NMR (400 MHz, $C_6D_6$) of ***5c***



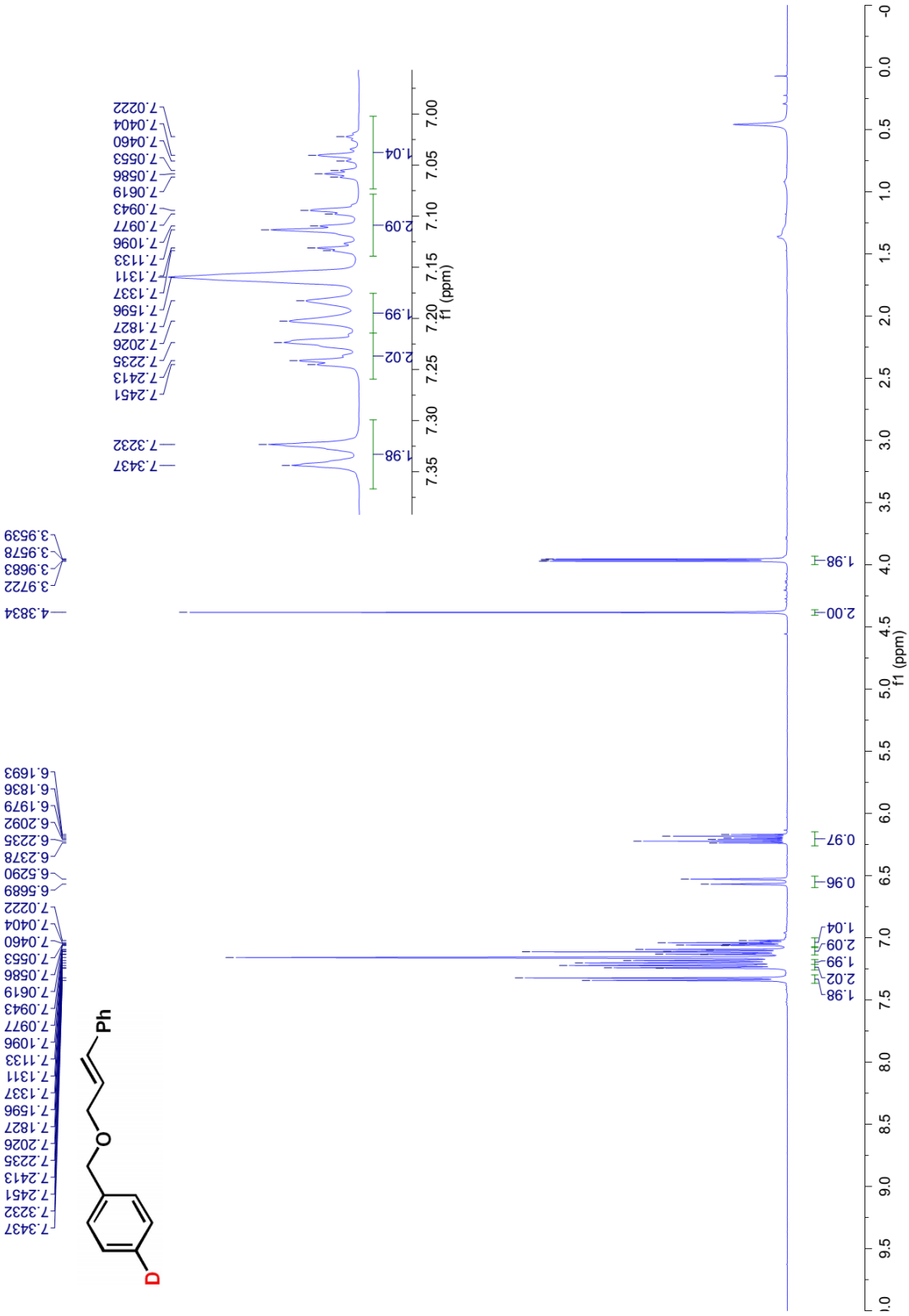

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***5c***



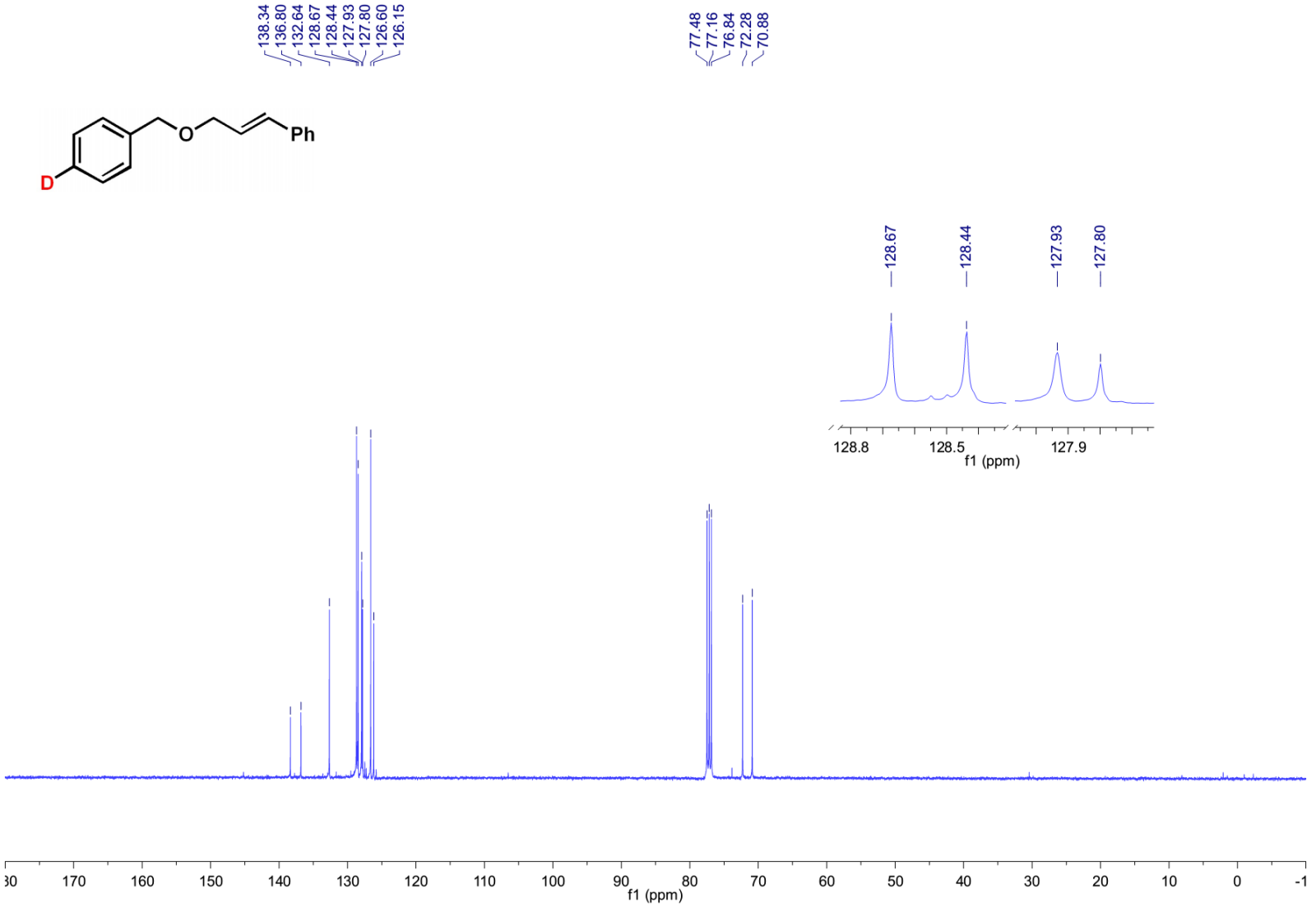

$^1$H NMR (400 MHz, $CDCl_3$) of ***5d***



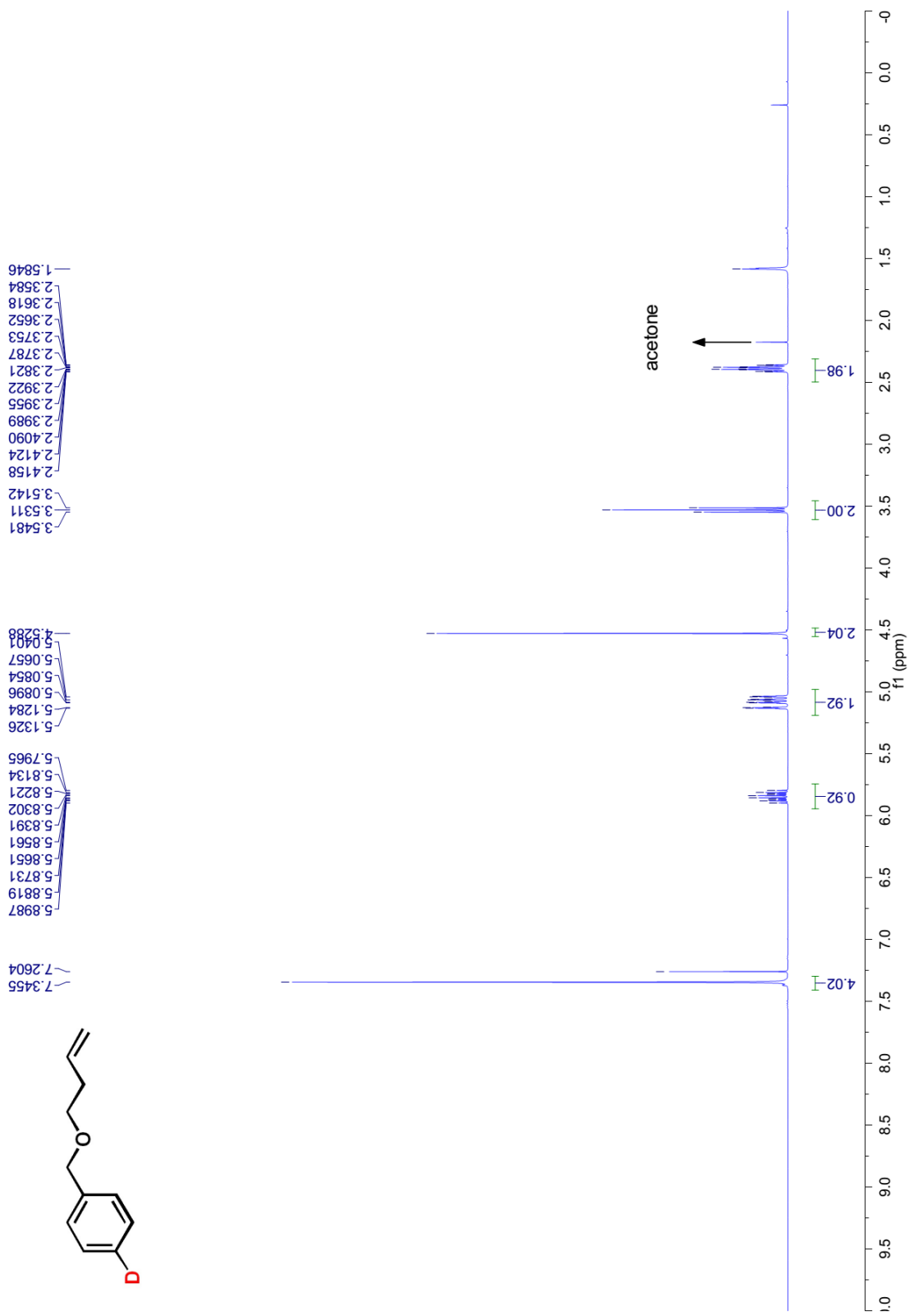

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***5d***



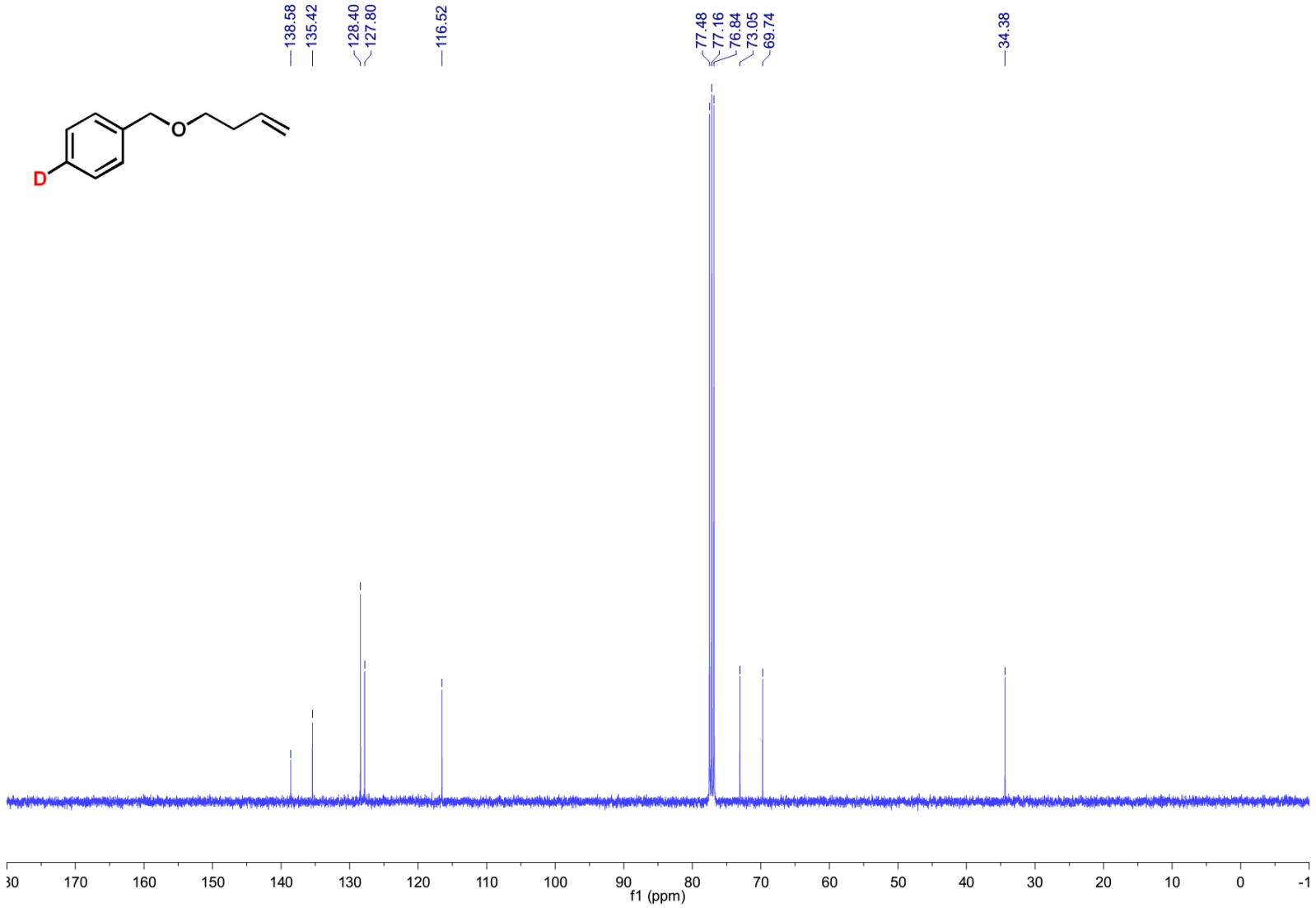

$^1$H NMR (400 MHz, $C_6D_6$) of ***5e***



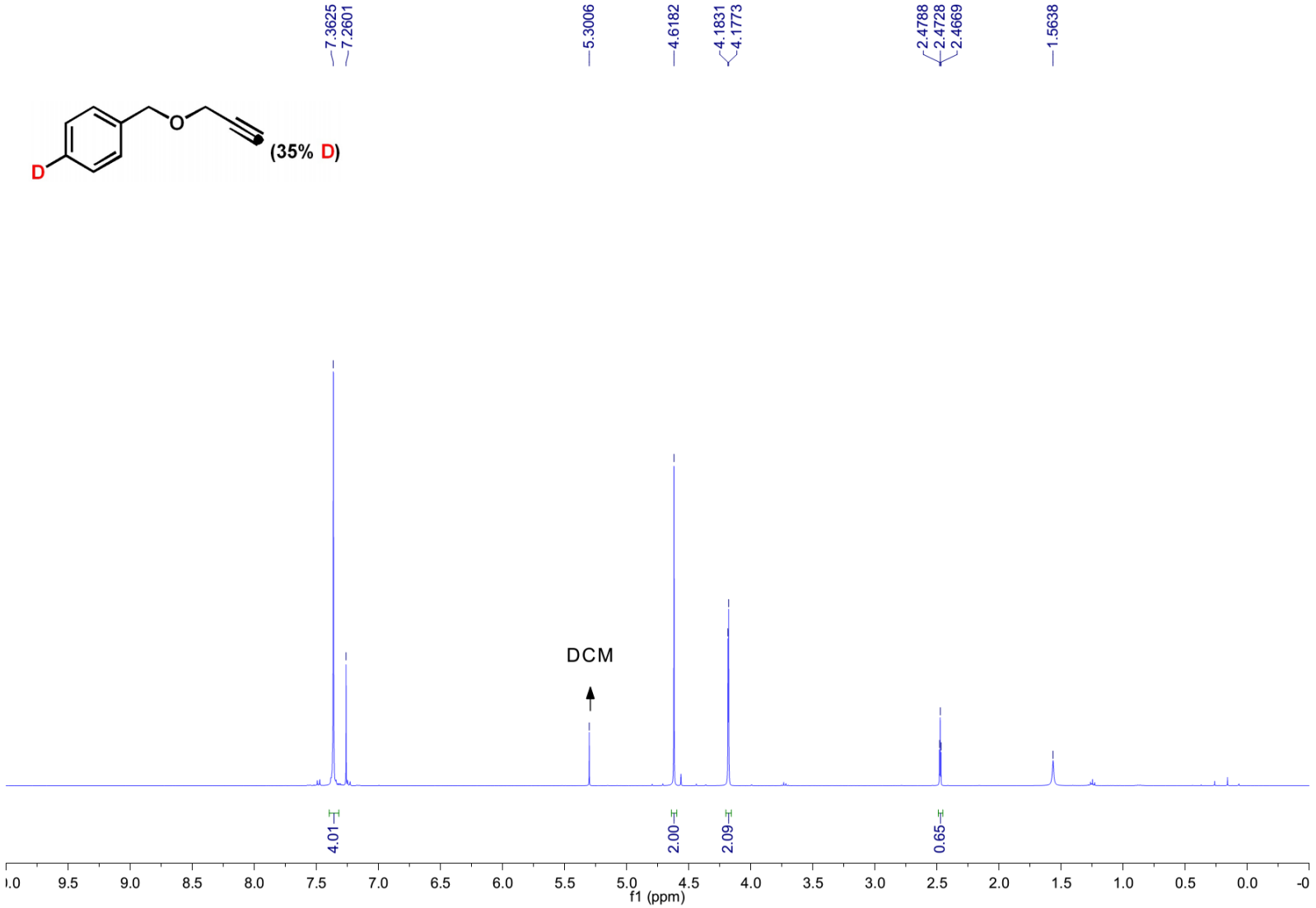

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***5e***



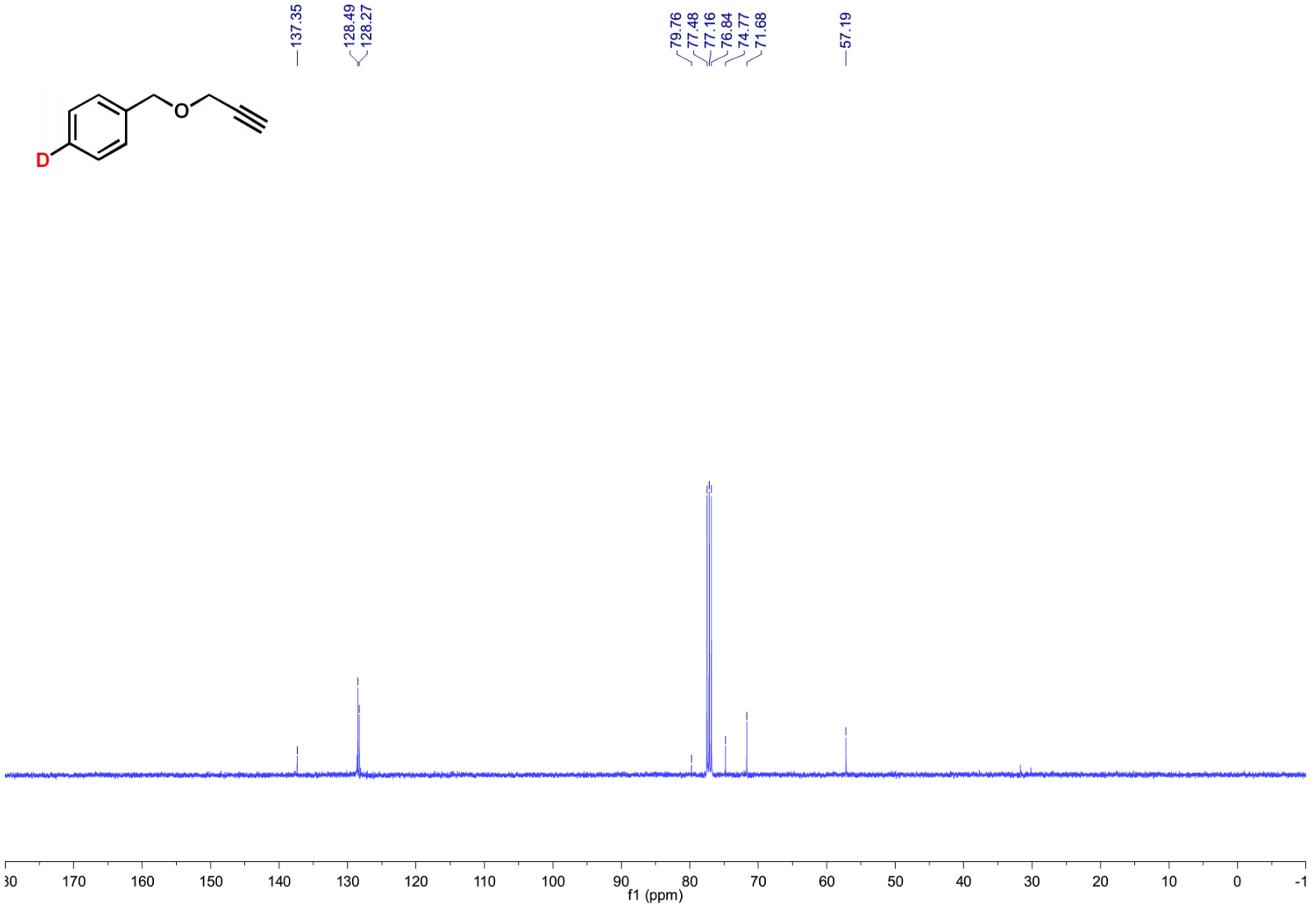

$^1$H NMR (400 MHz, $CDCl_3$) of ***5f***



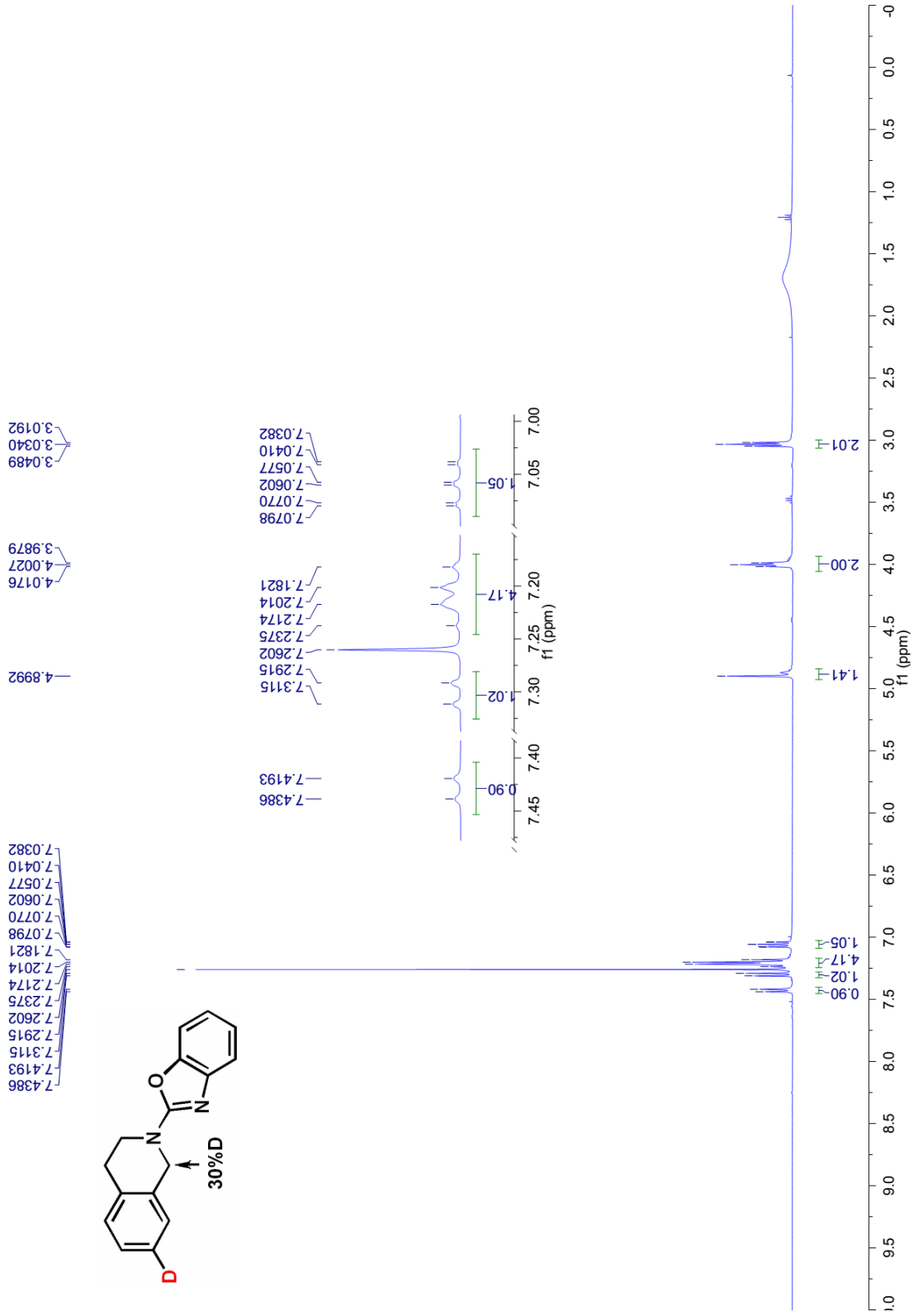

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***5f***



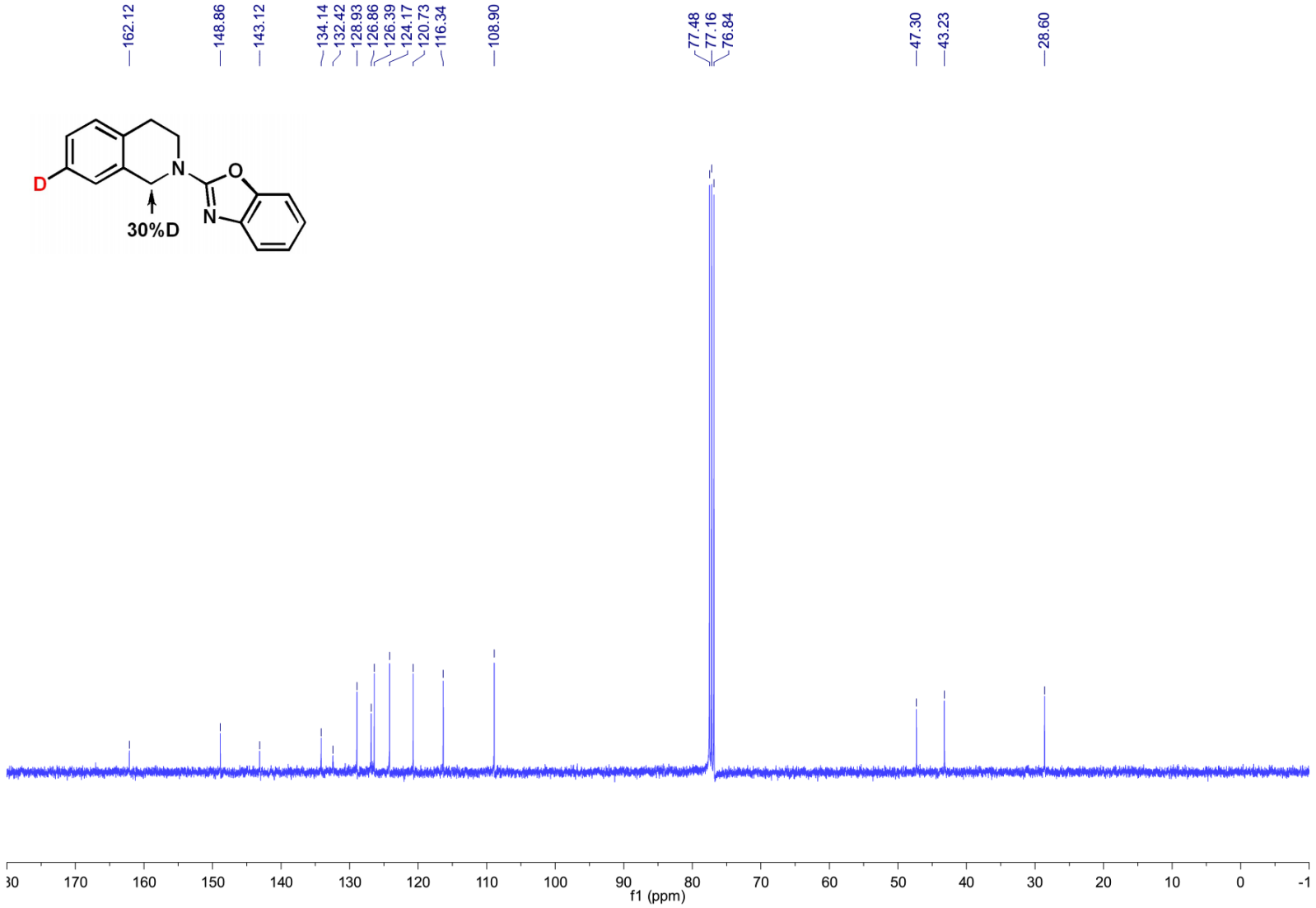

$^{1}$H NMR (400 MHz, $CDCl_3$) of ***5g***



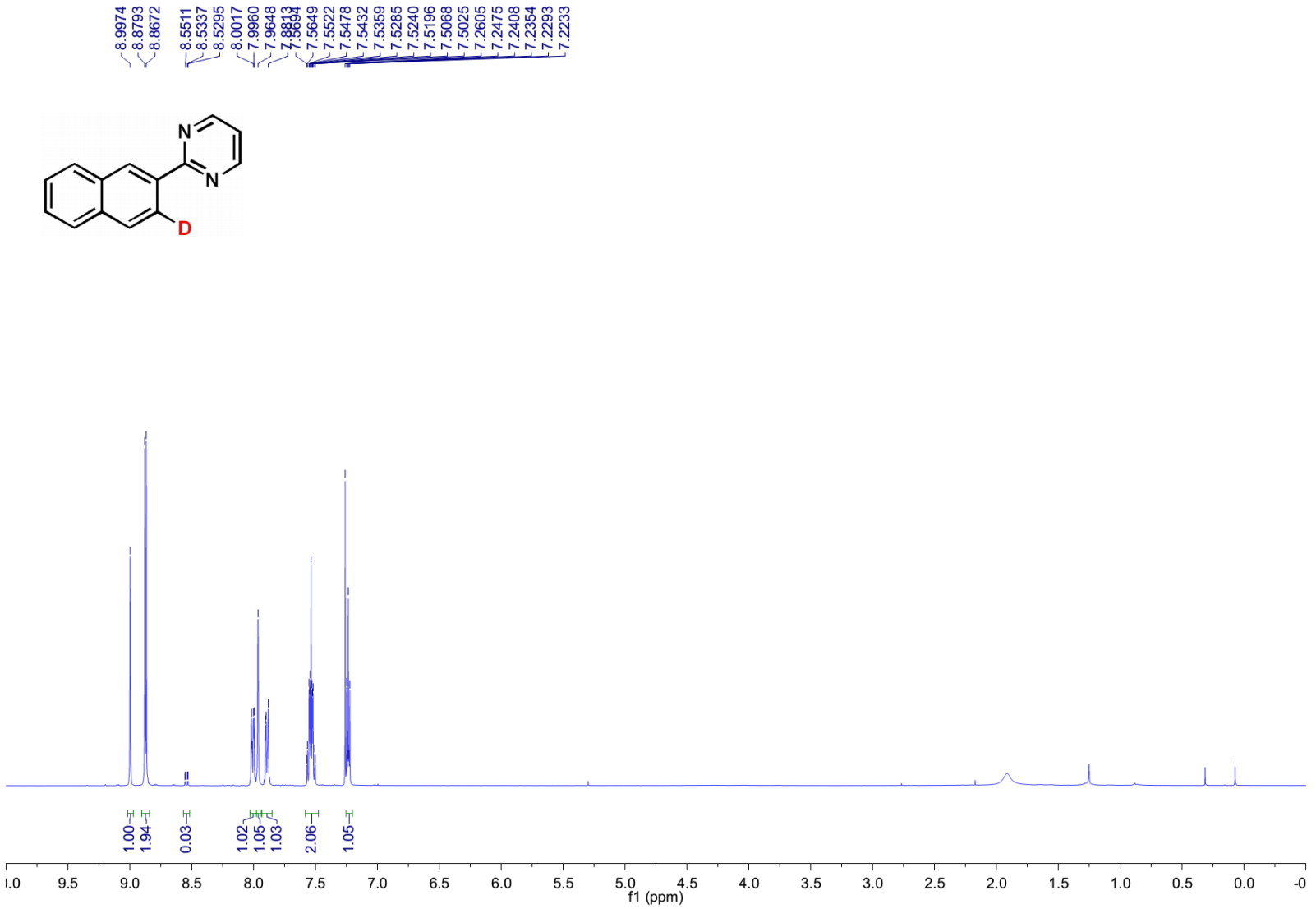

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***5g***



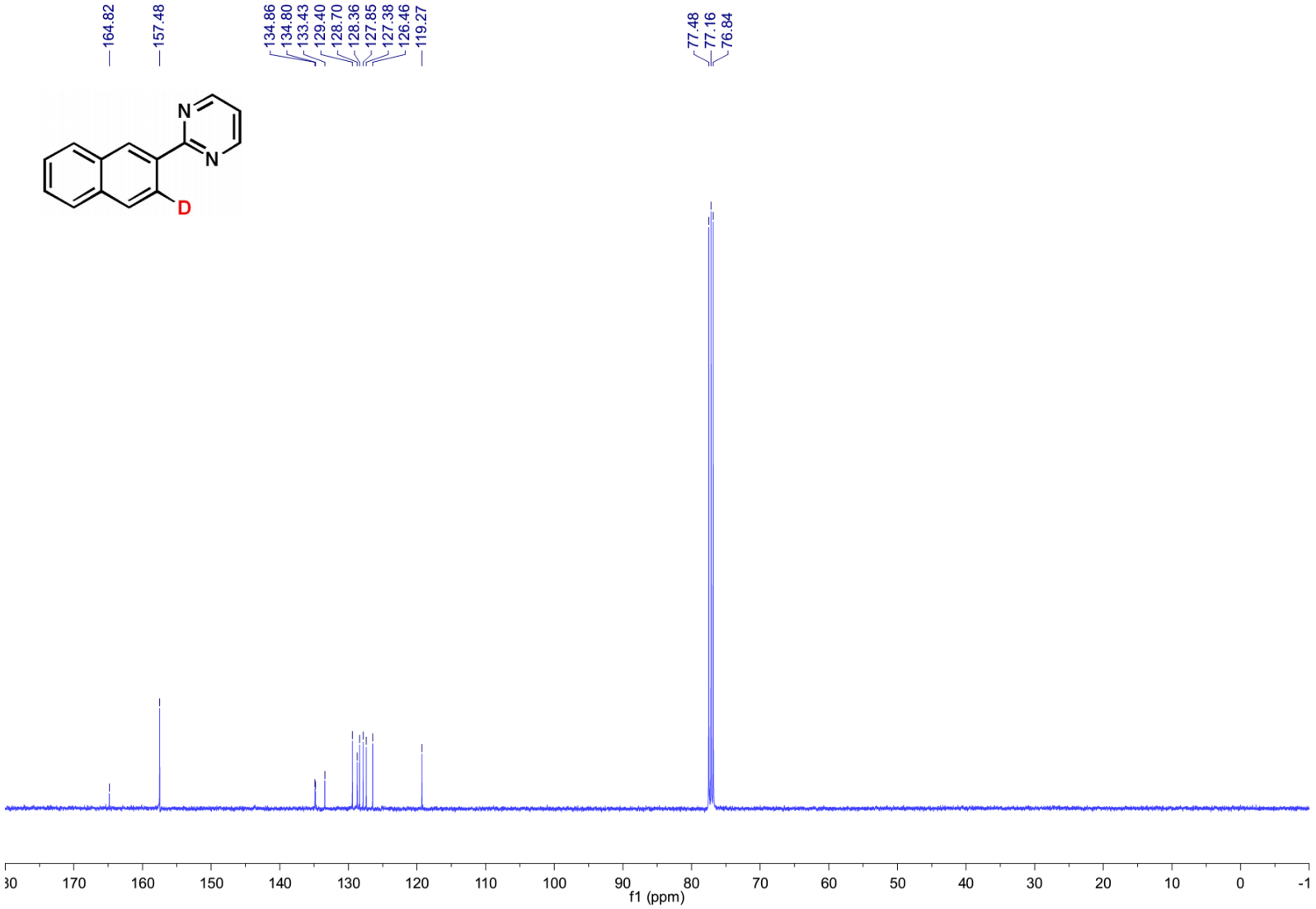

$^1$H NMR (400 MHz, $CDCl_3$) of ***6a***



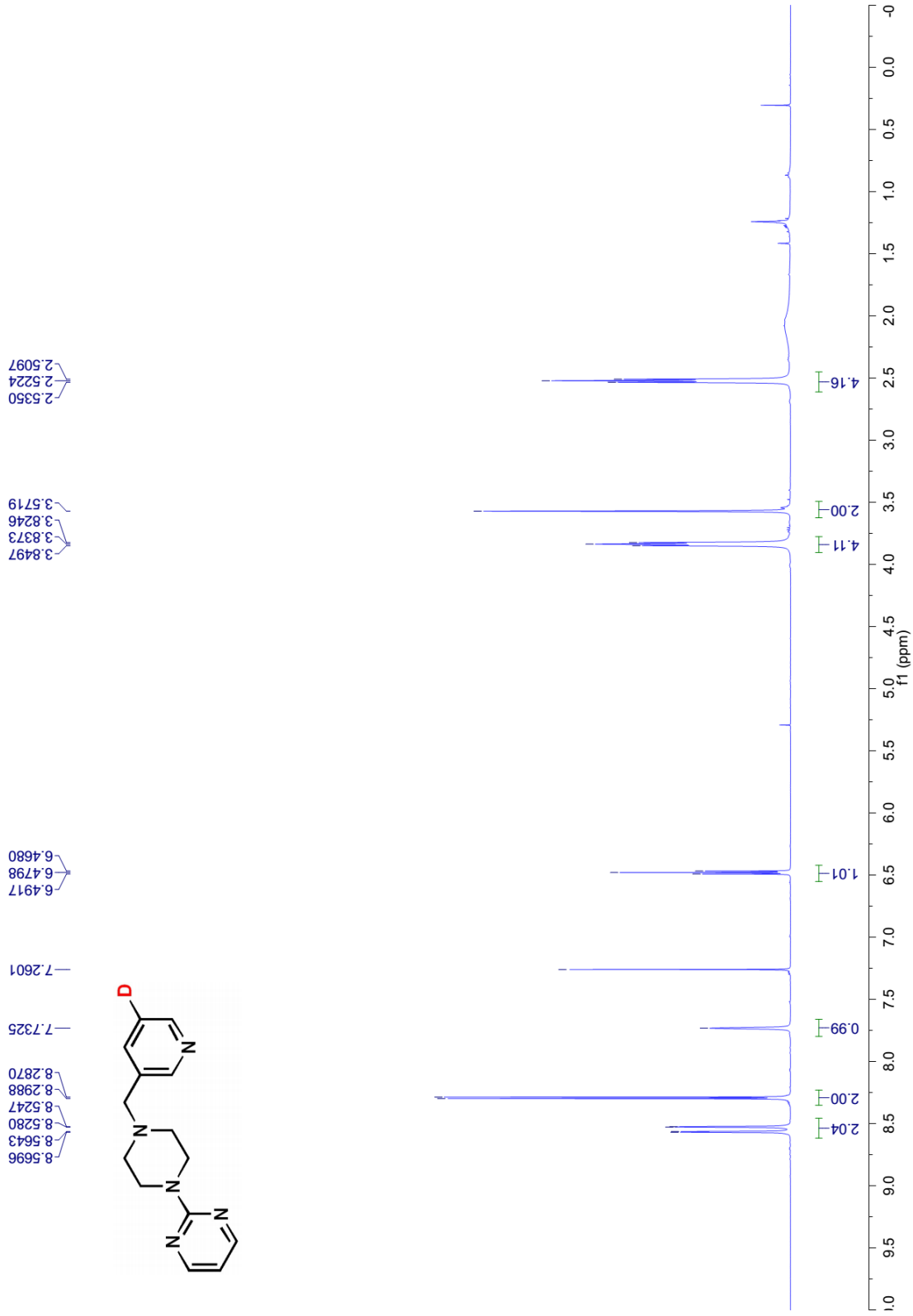

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***6a***



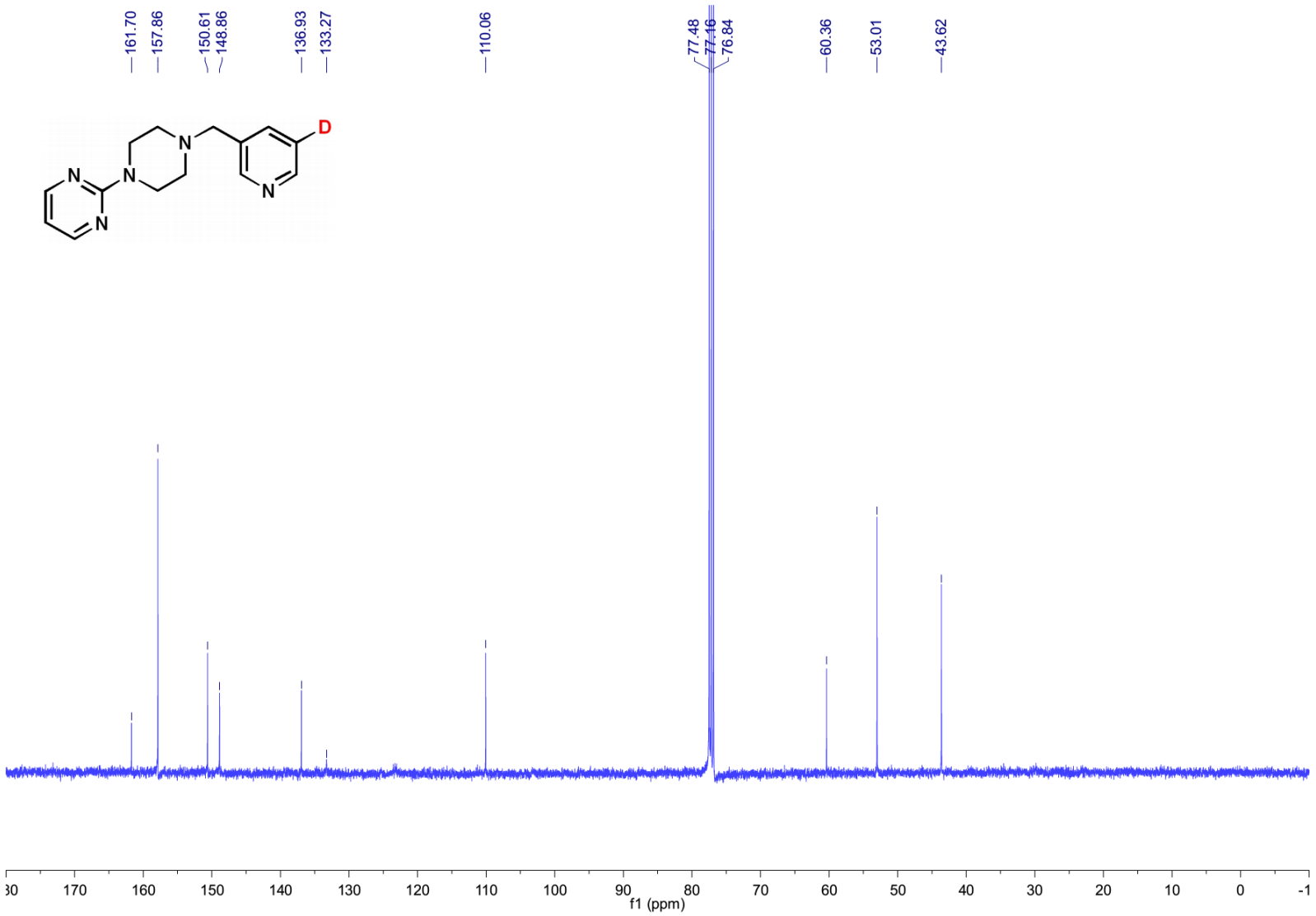

$^{1}$H NMR (400 MHz, $CDCl_3$) of ***6b***



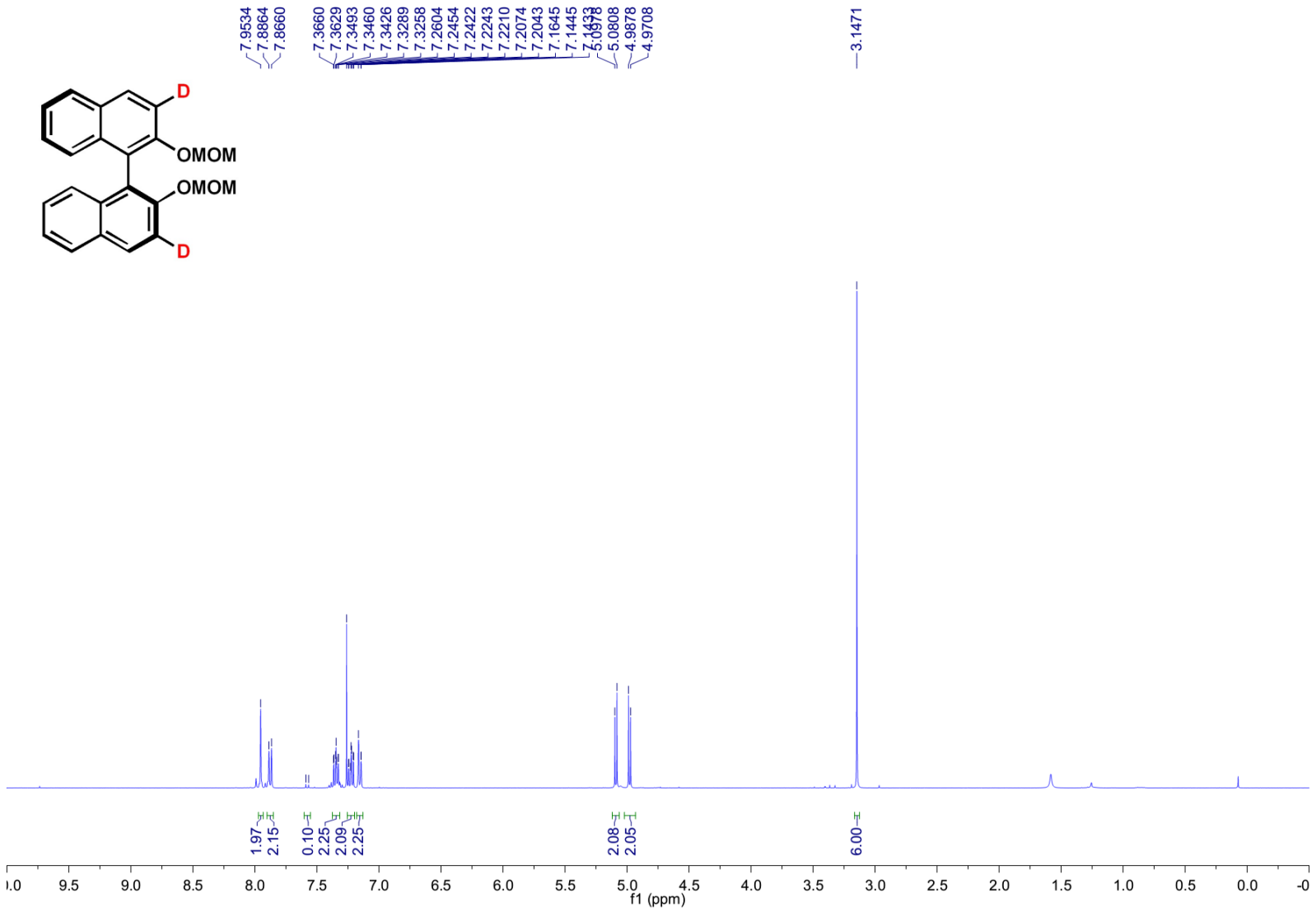

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***6b***



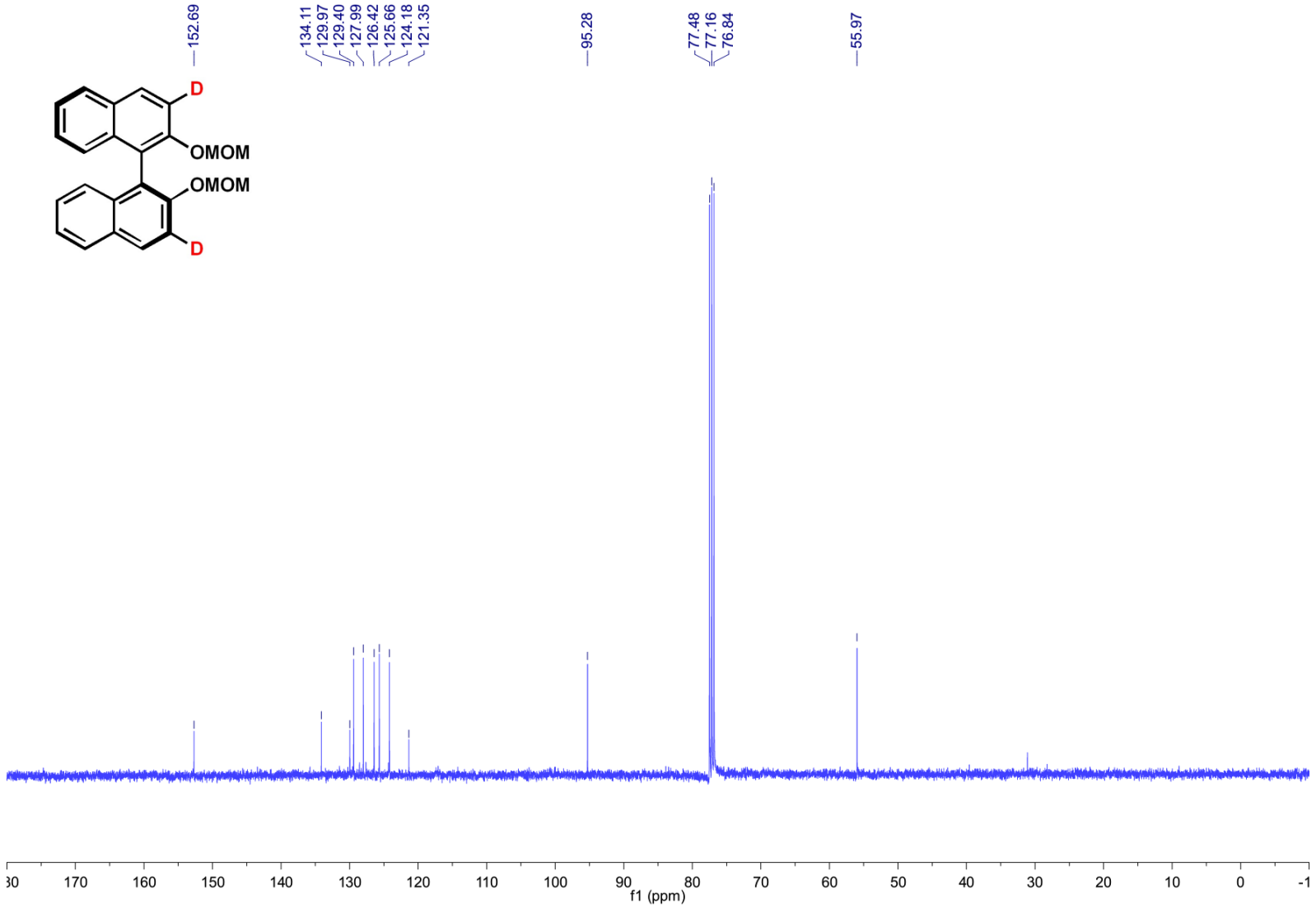

$^1$H NMR (400 MHz, $CDCl_3$) of ***6c***



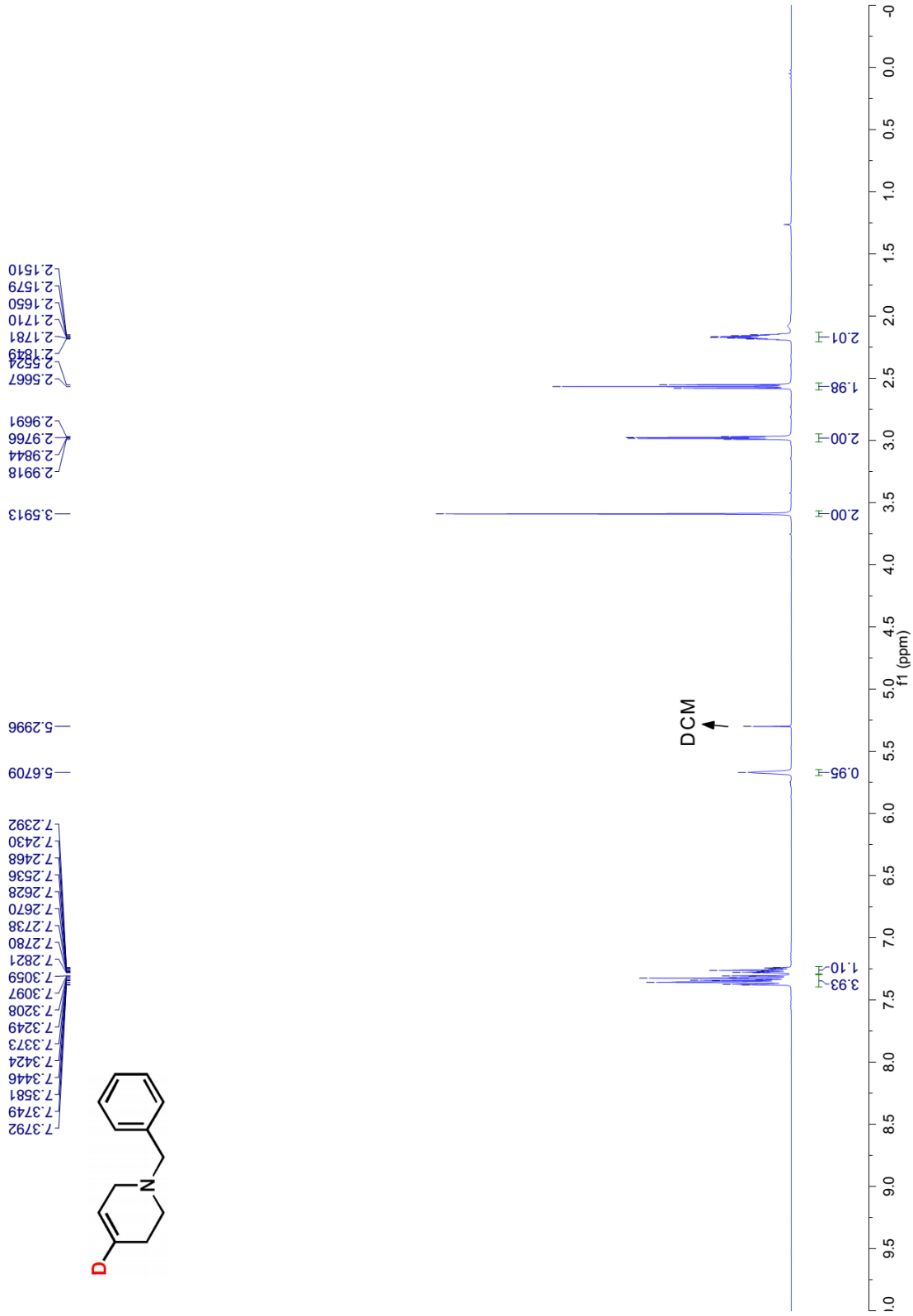

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***6c***



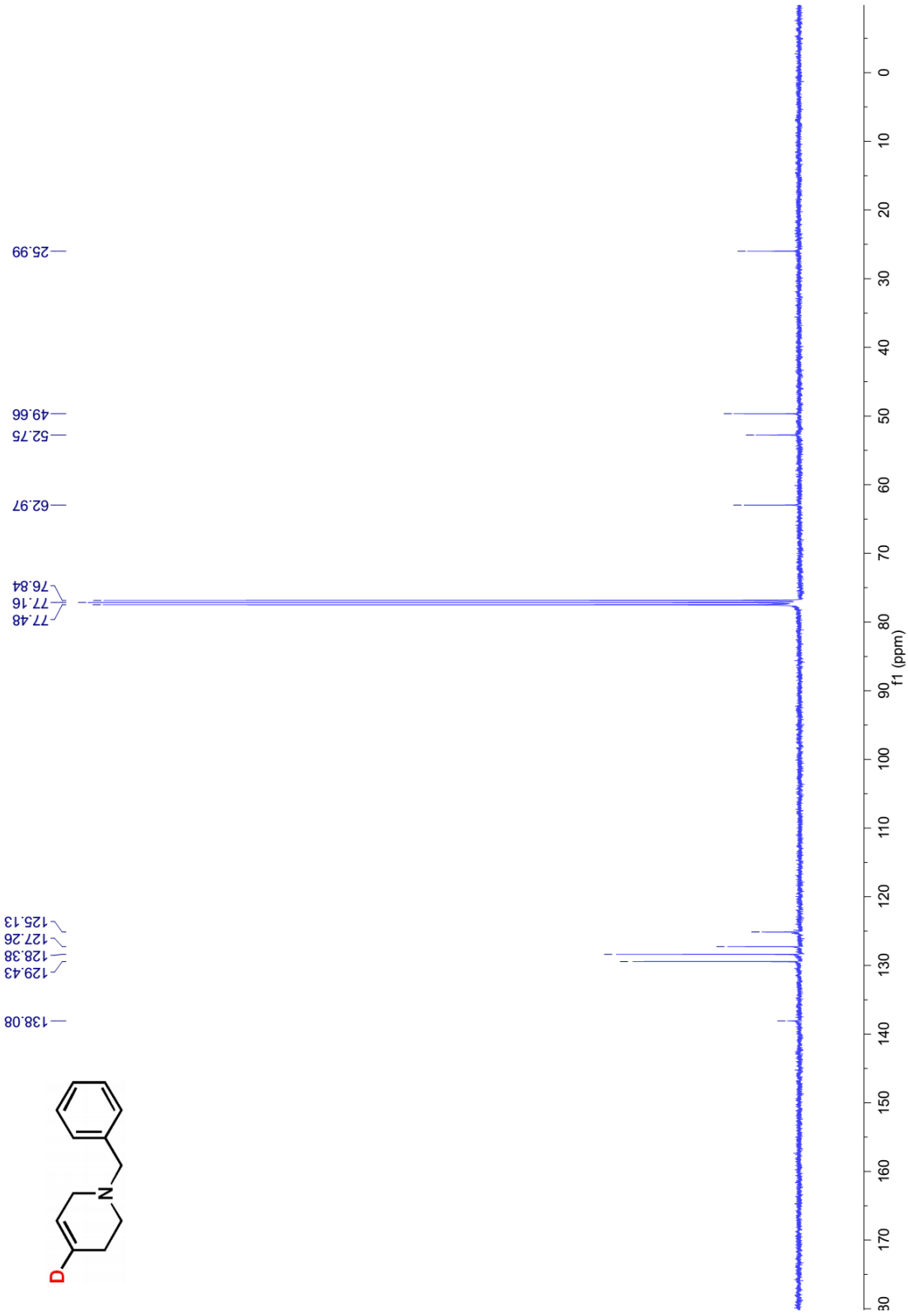

$^{1}$H NMR (400 MHz, $CDCl_3$) of ***6d***



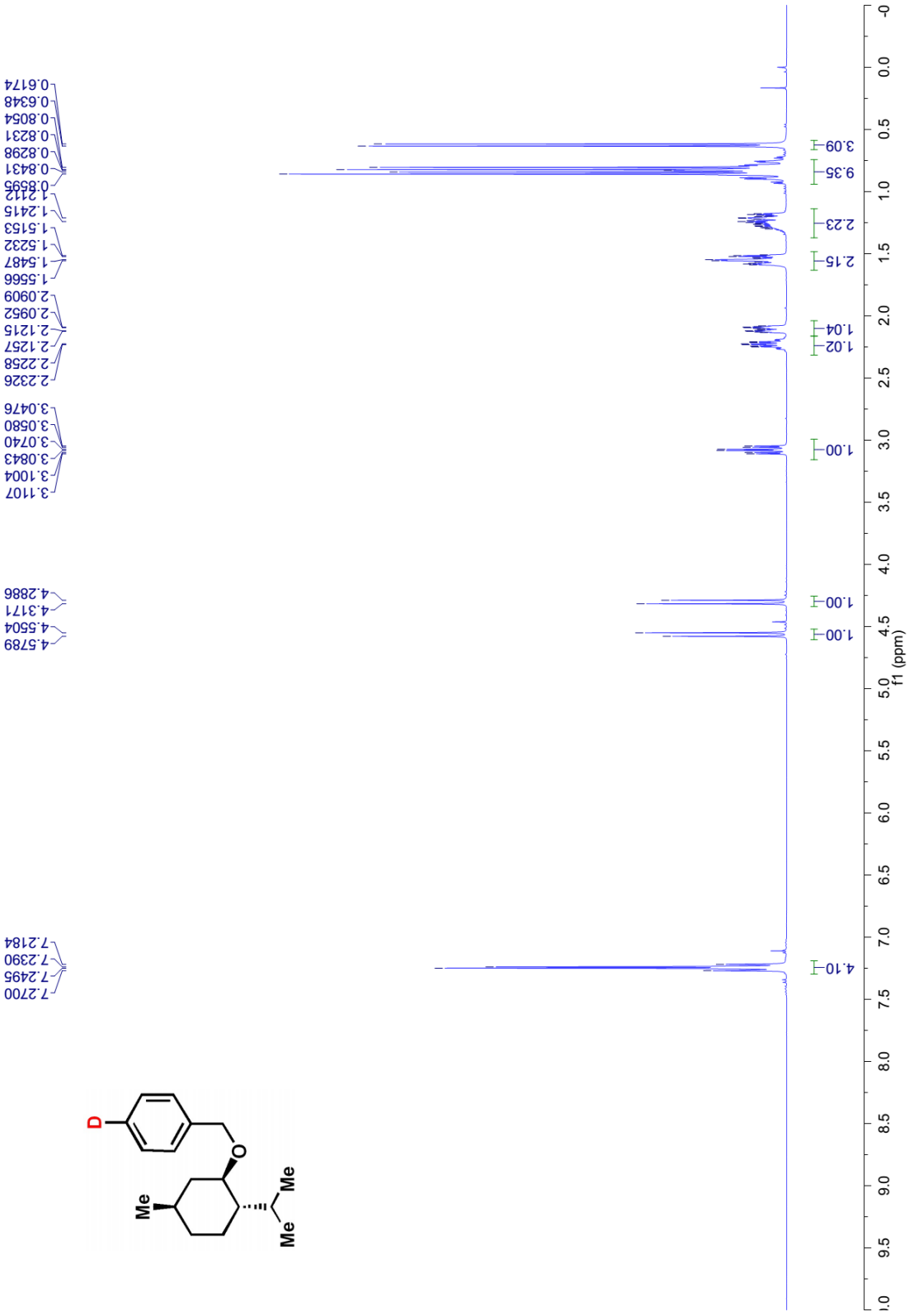

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***6d***



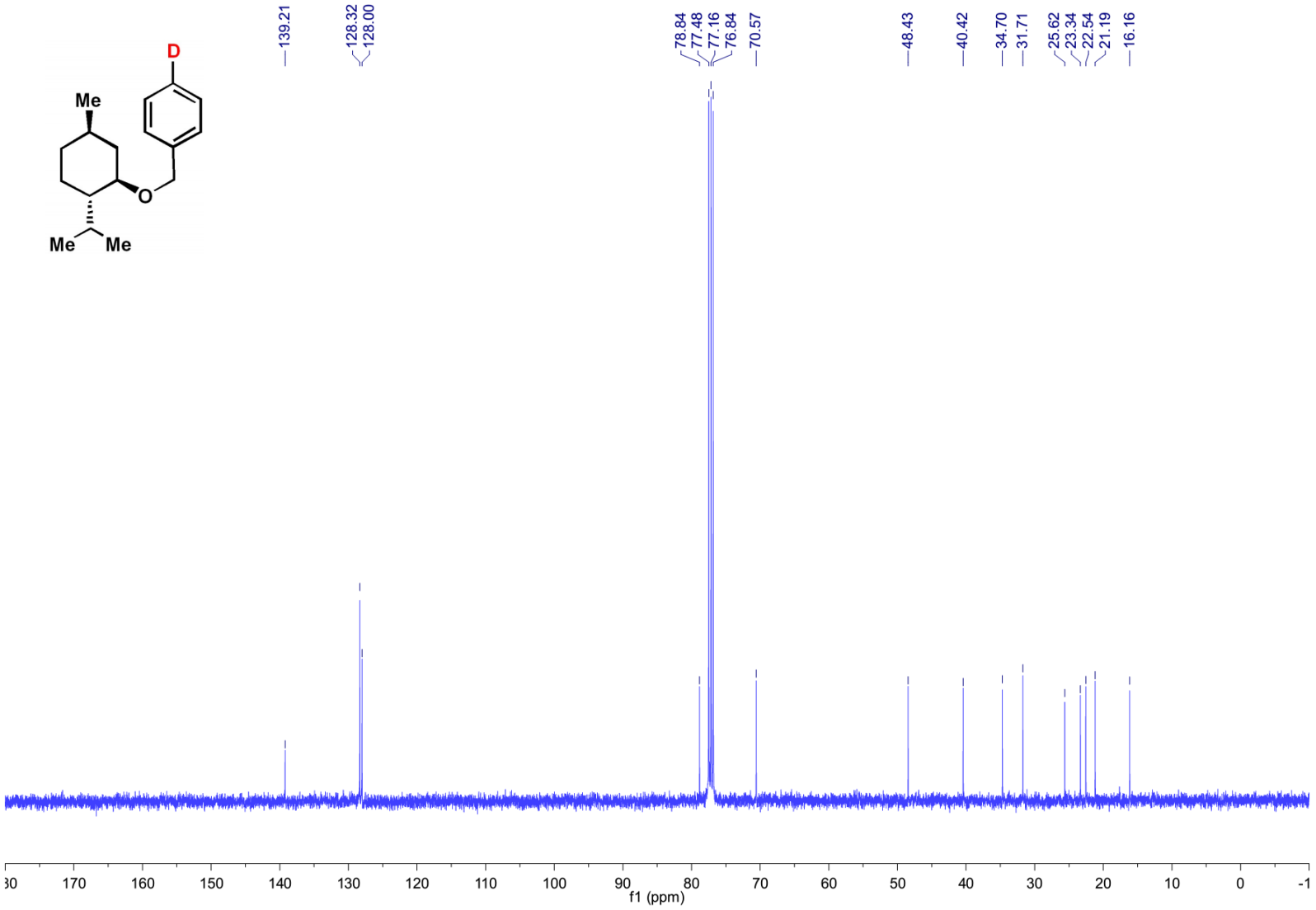

$^1$H NMR (400 MHz, $CDCl_3$) of ***6e***



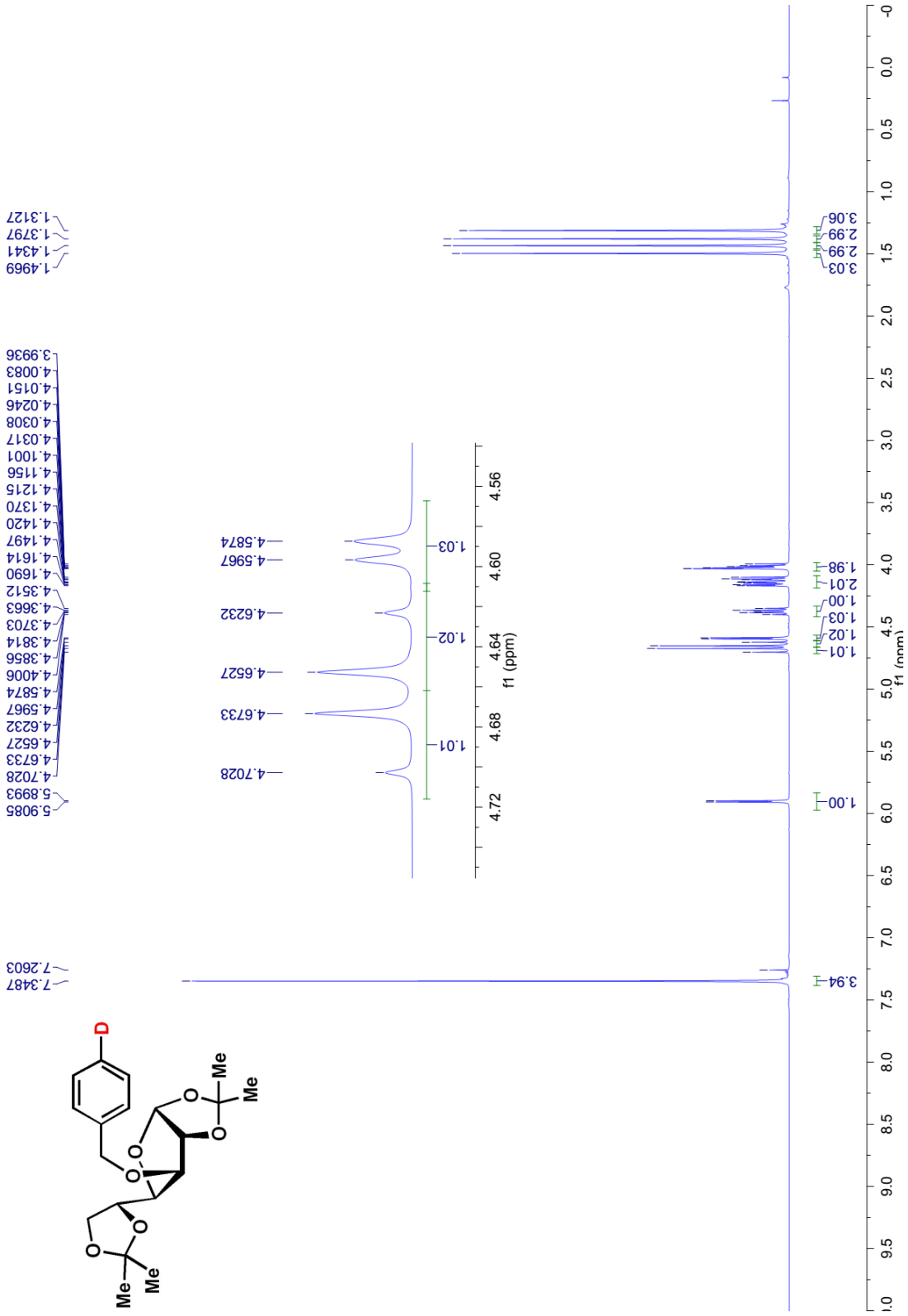

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***6e***



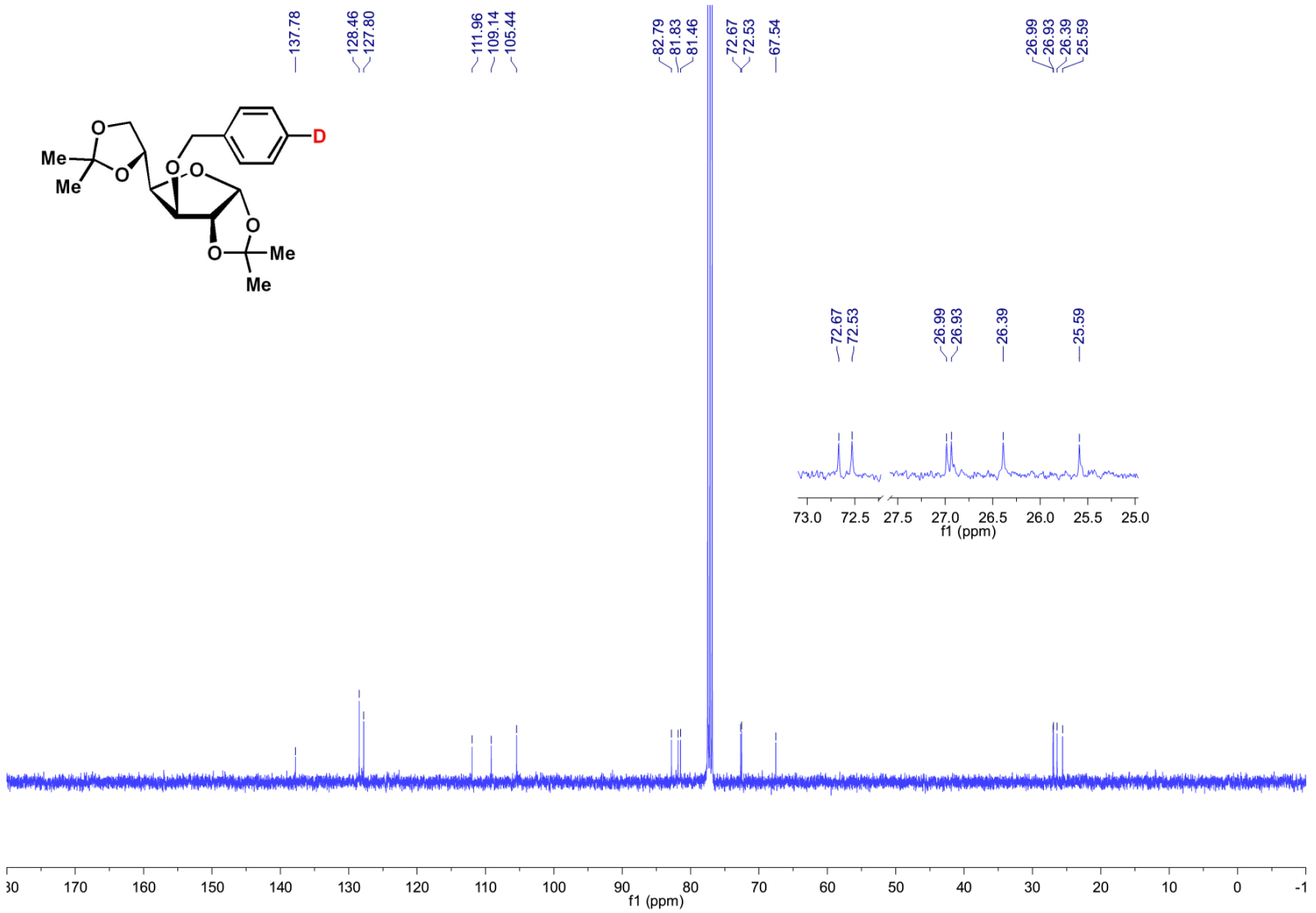

$^1$H NMR (400 MHz, $CDCl_3$) of ***7a***



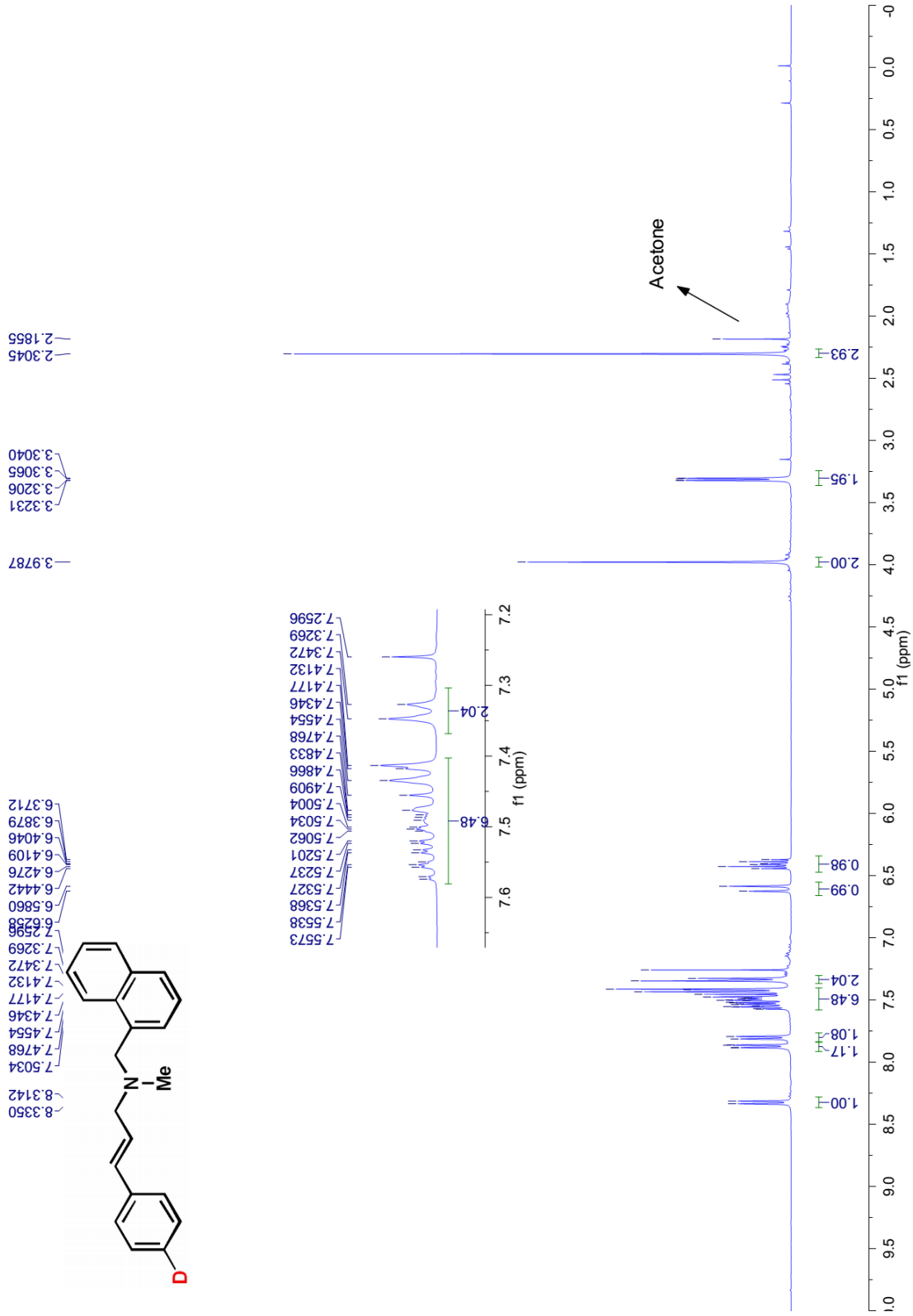

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***7a***



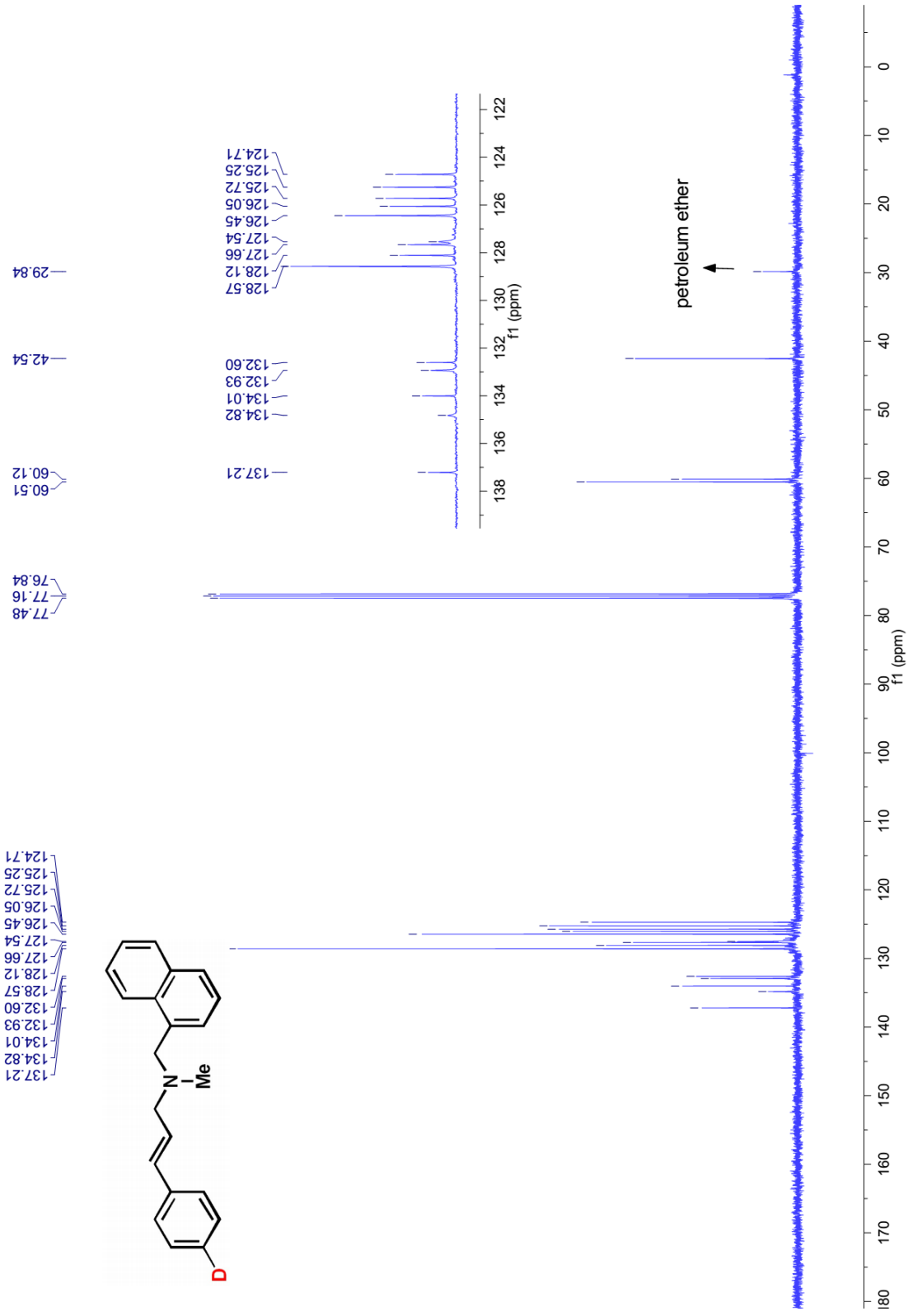

$^1$H NMR (400 MHz, $CDCl_3$) of ***7b***



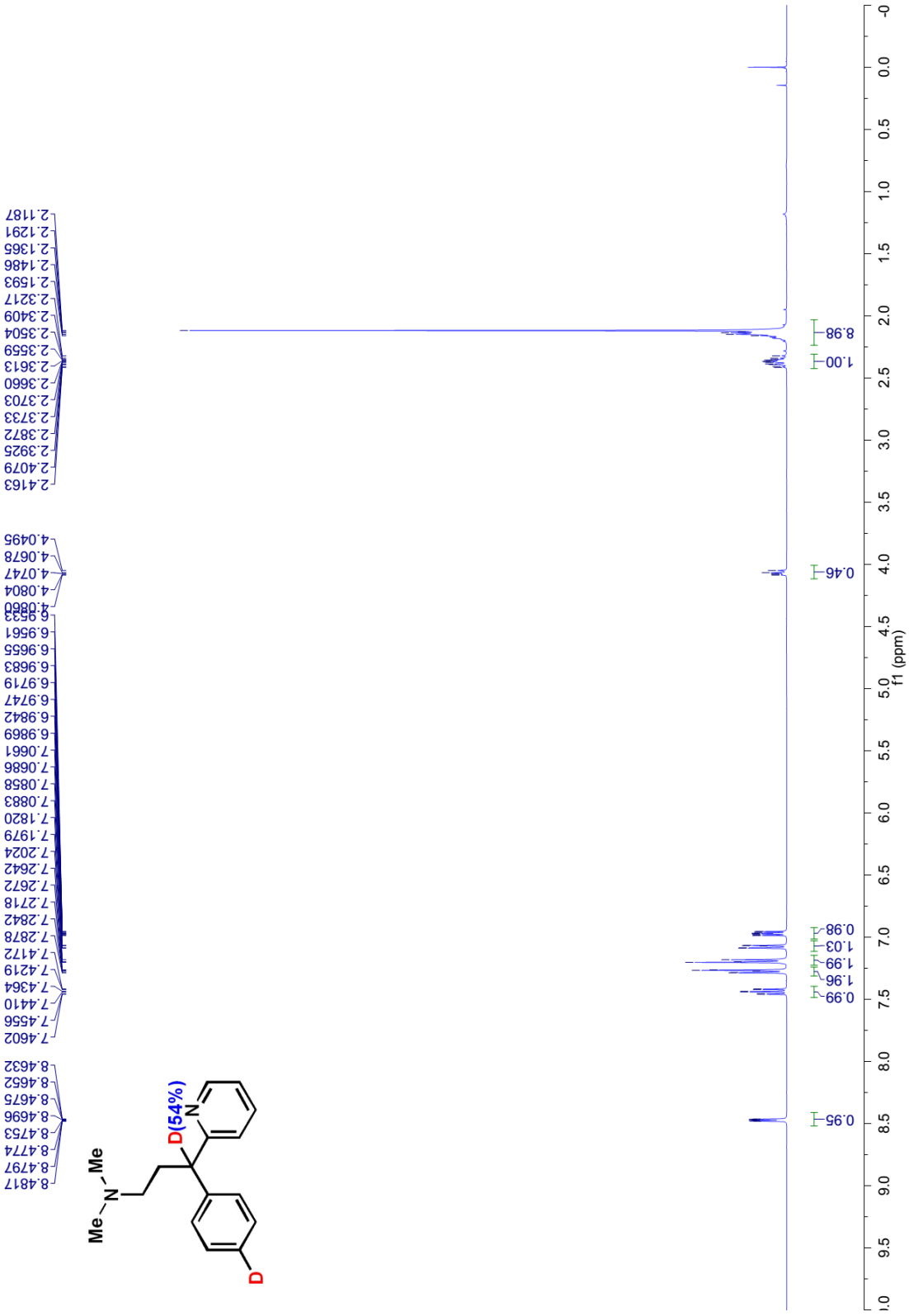

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***7b***



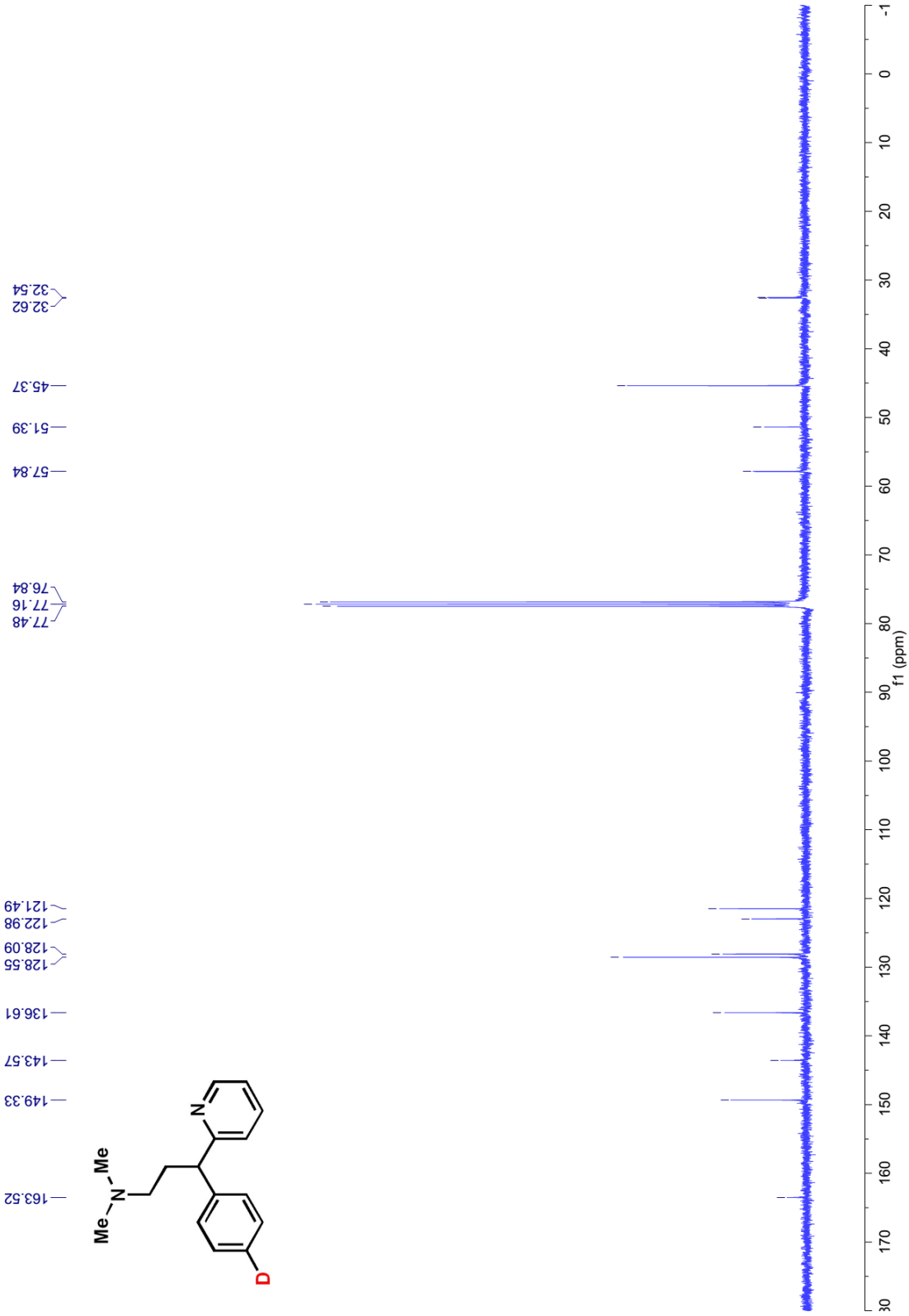

$^1$H NMR (400 MHz, $CDCl_3$) of ***7c***



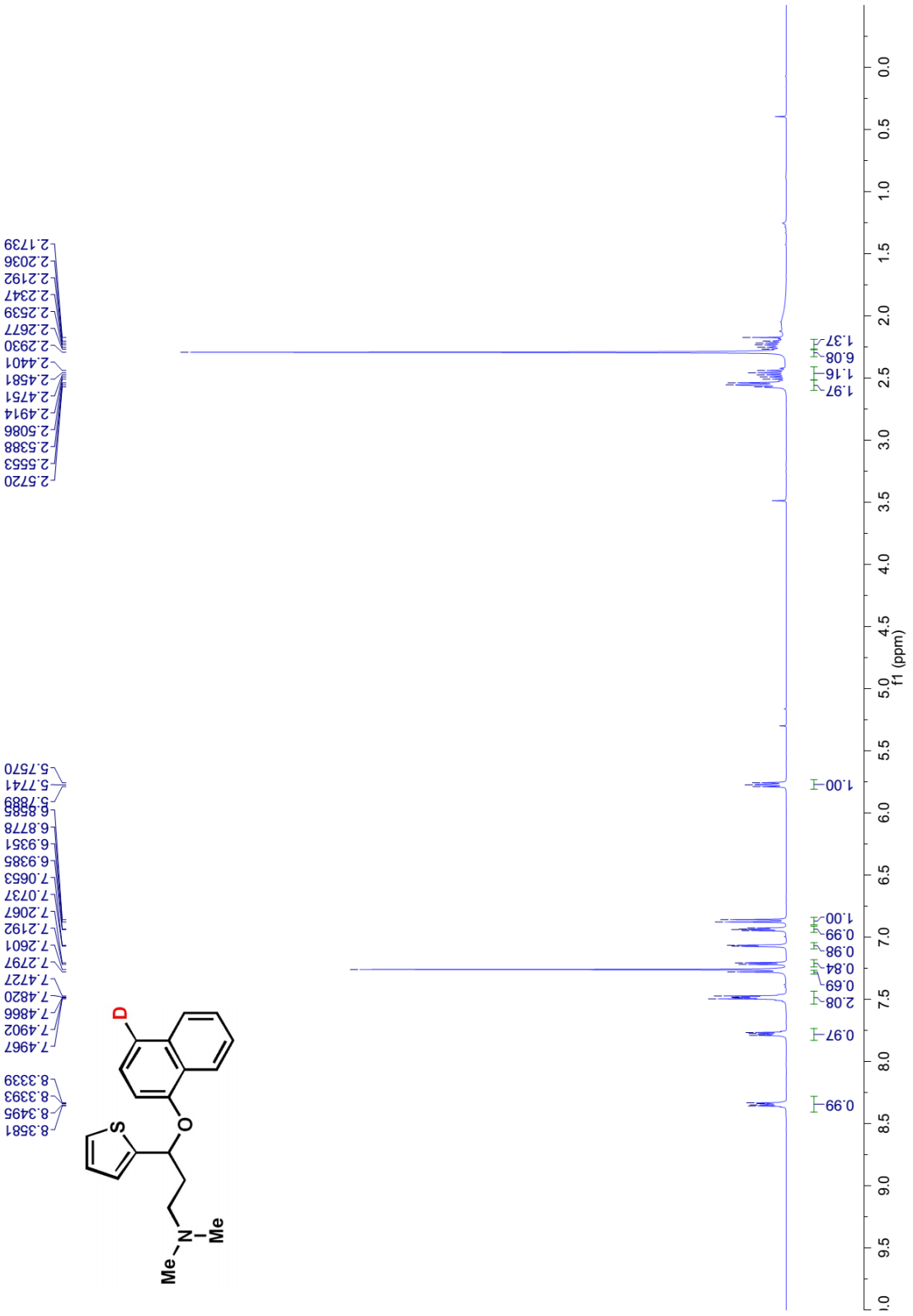

$^{13}$C NMR (100 MHz, $CDCl_3$) of **7c**



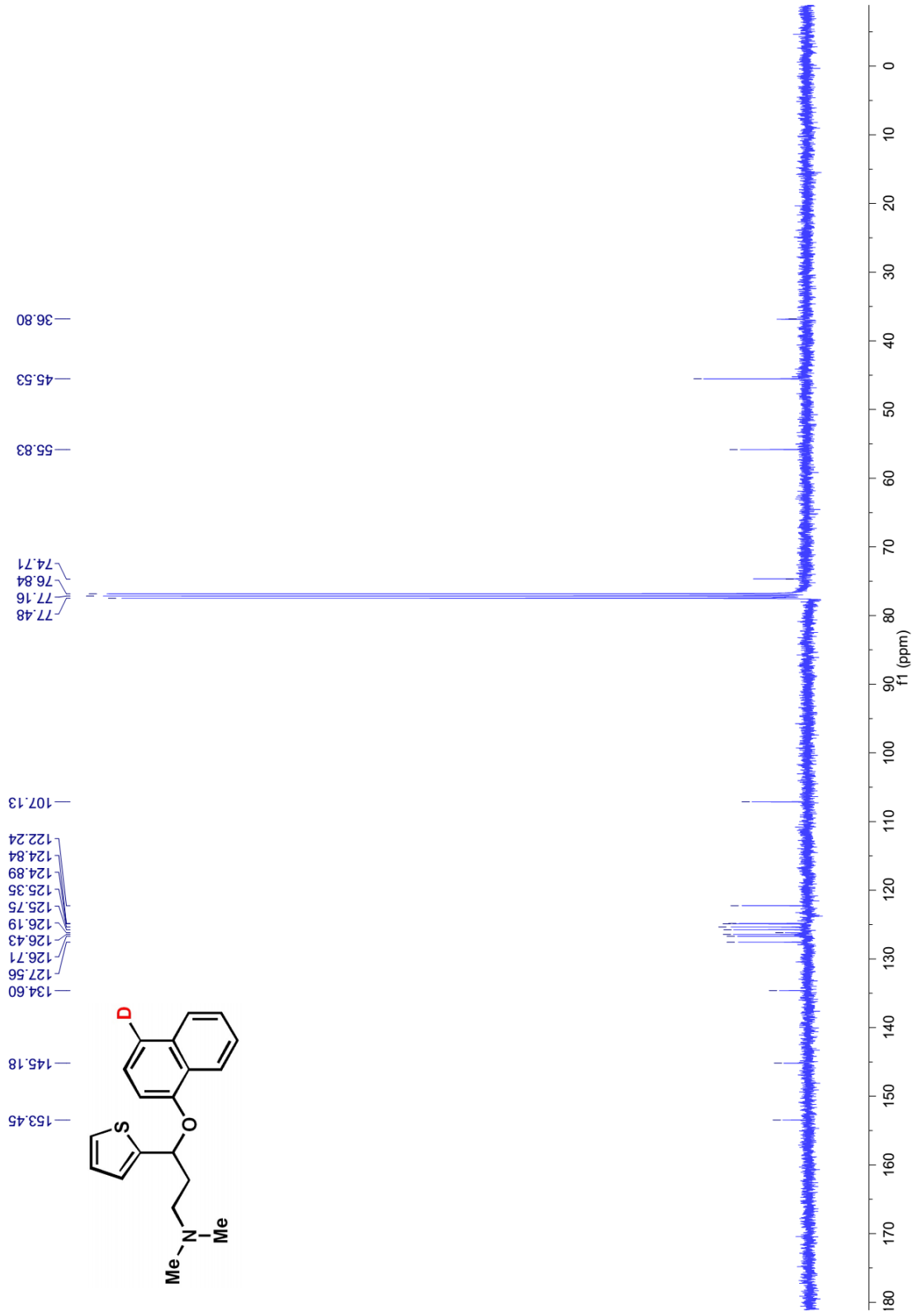

$^1$H NMR (400 MHz, $CDCl_3$) of ***7d***



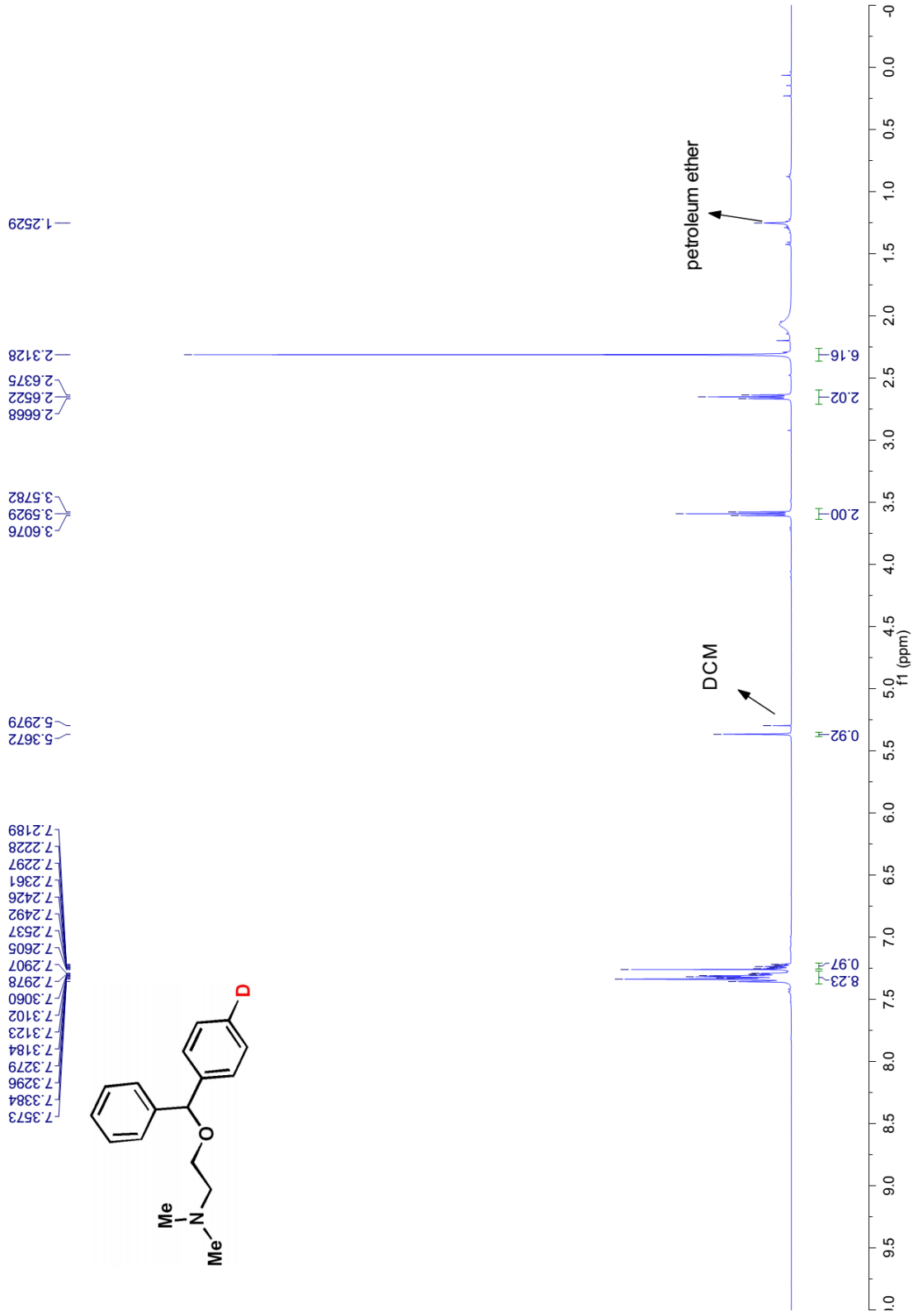

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***7d***



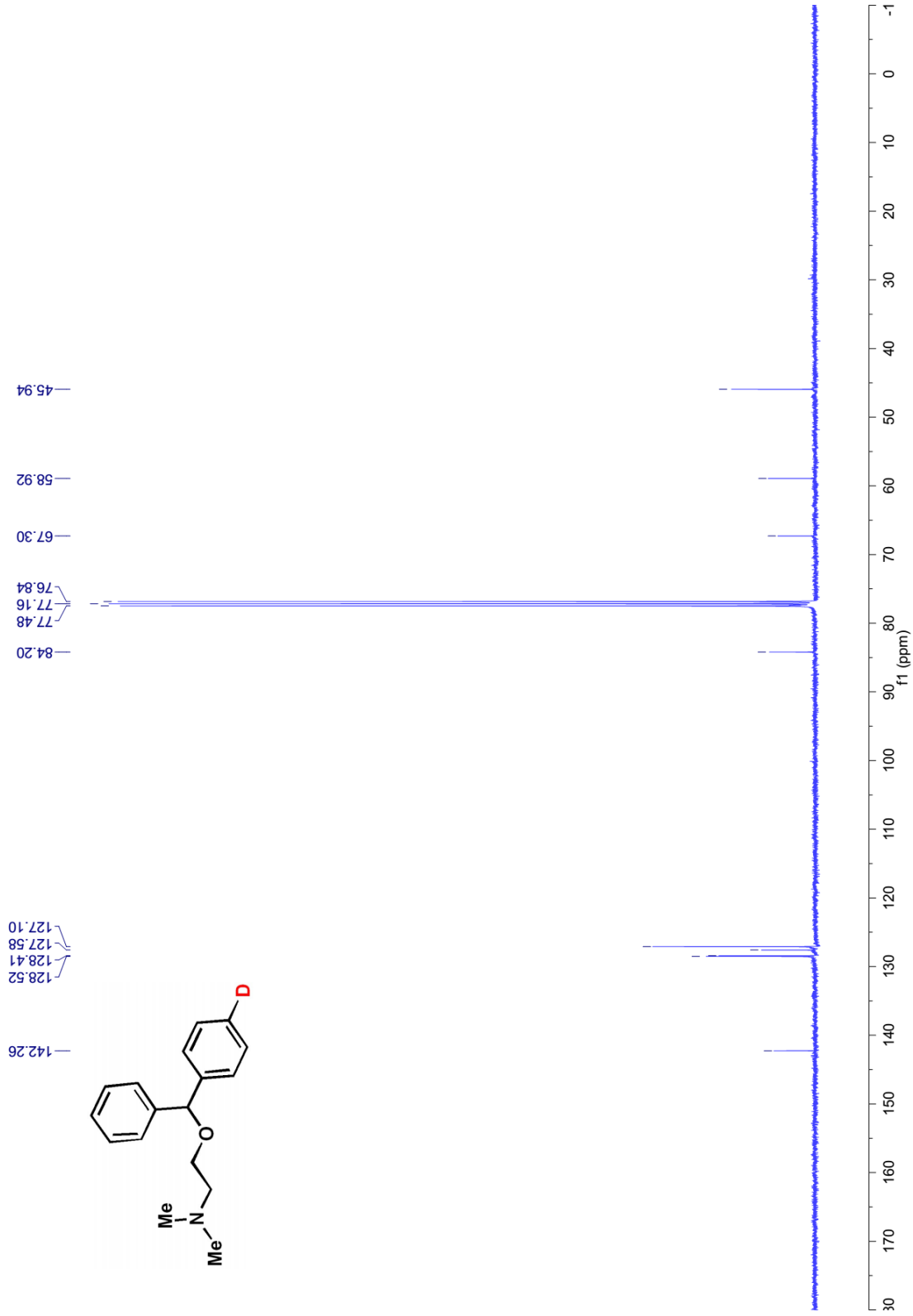

$^1$H NMR (400 MHz, $CDCl_3$) of ***7e***



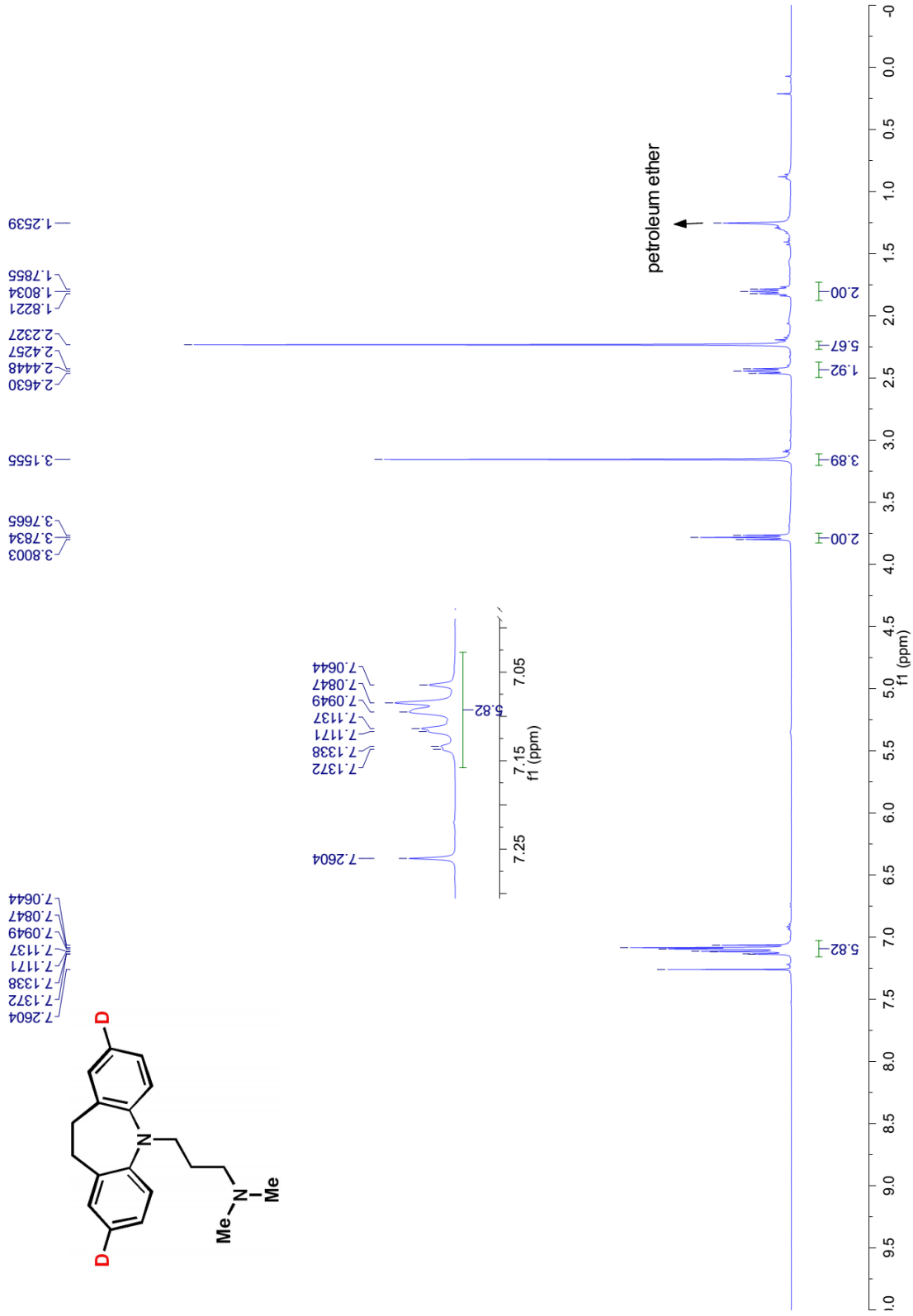

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***7e***



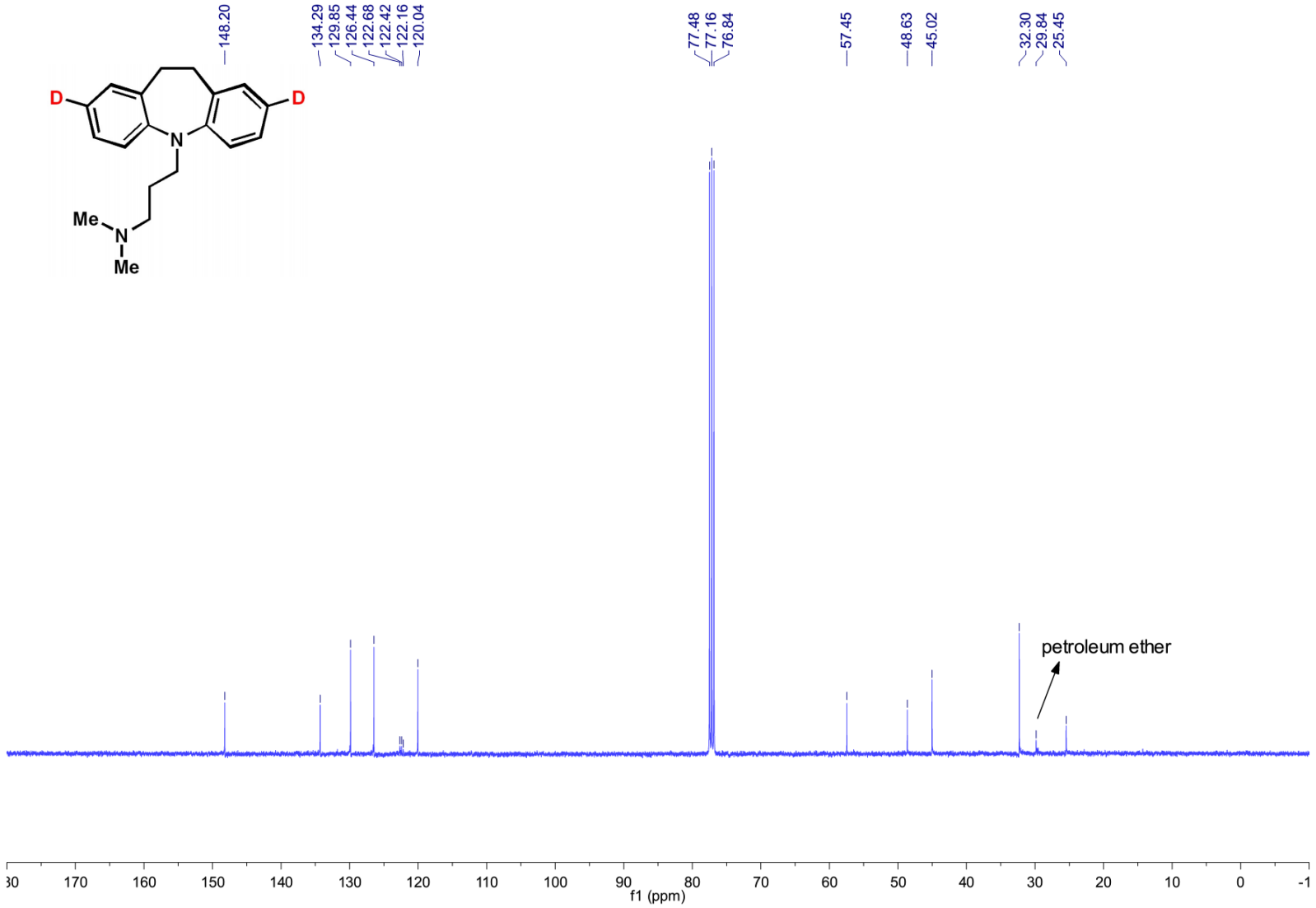

$^1$H NMR (400 MHz, $CDCl_3$) of ***7f***




$^{13}$C NMR (100 MHz, $CDCl_3$) of ***7f***

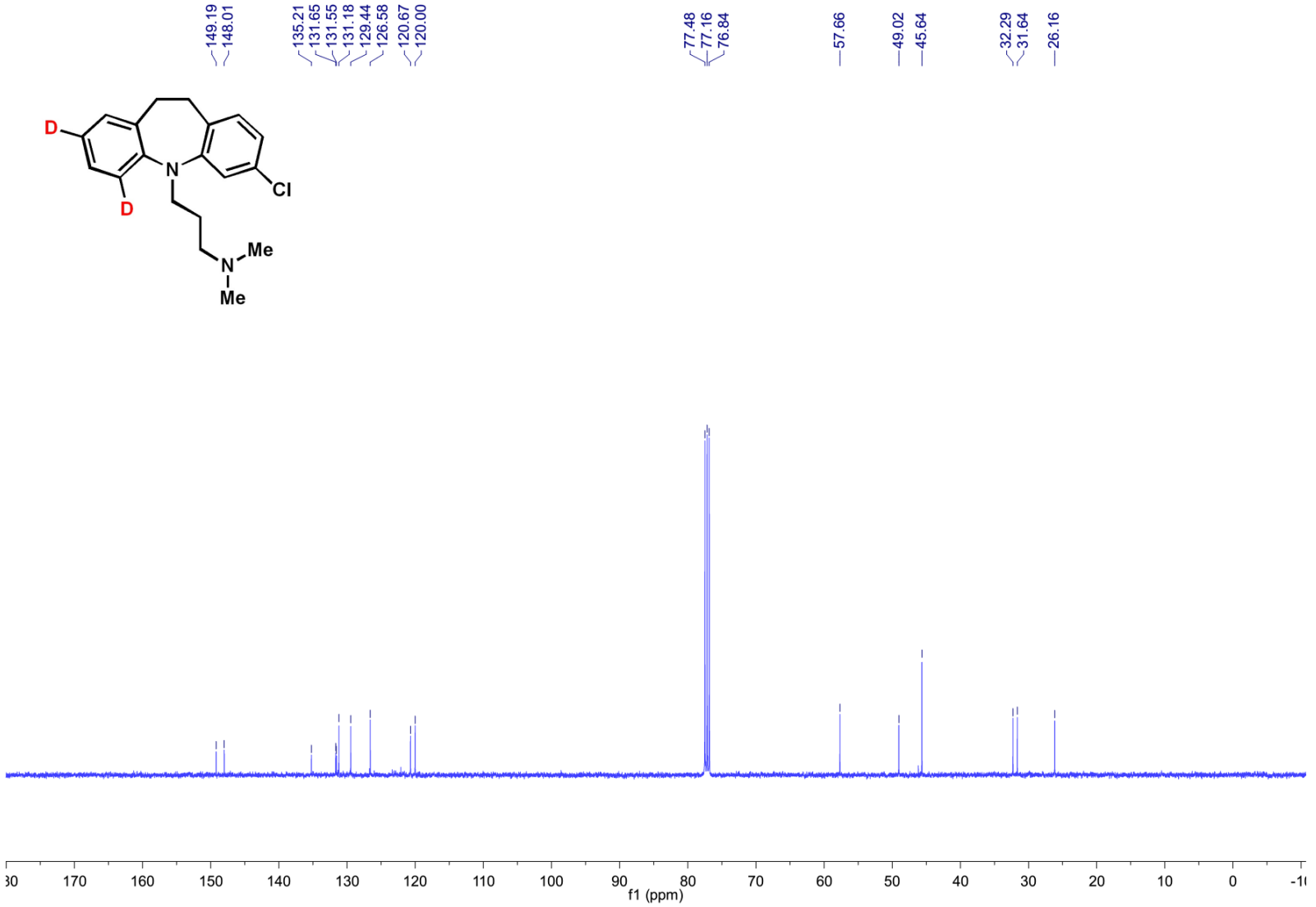



$^1$H NMR (400 MHz, $CDCl_3$) of ***7g***

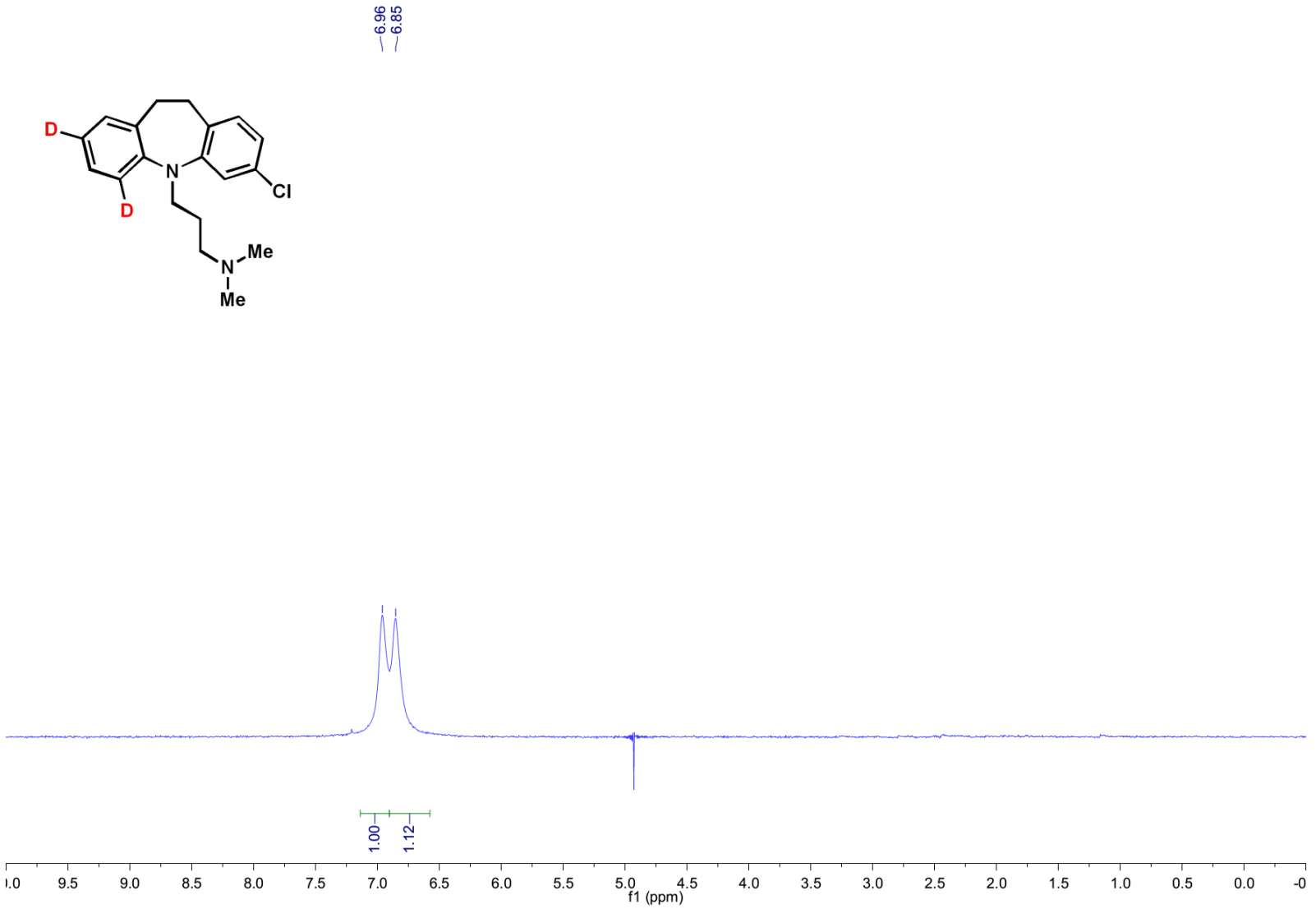



$^{13}$C NMR (100 MHz, $CDCl_3$) of ***7g***

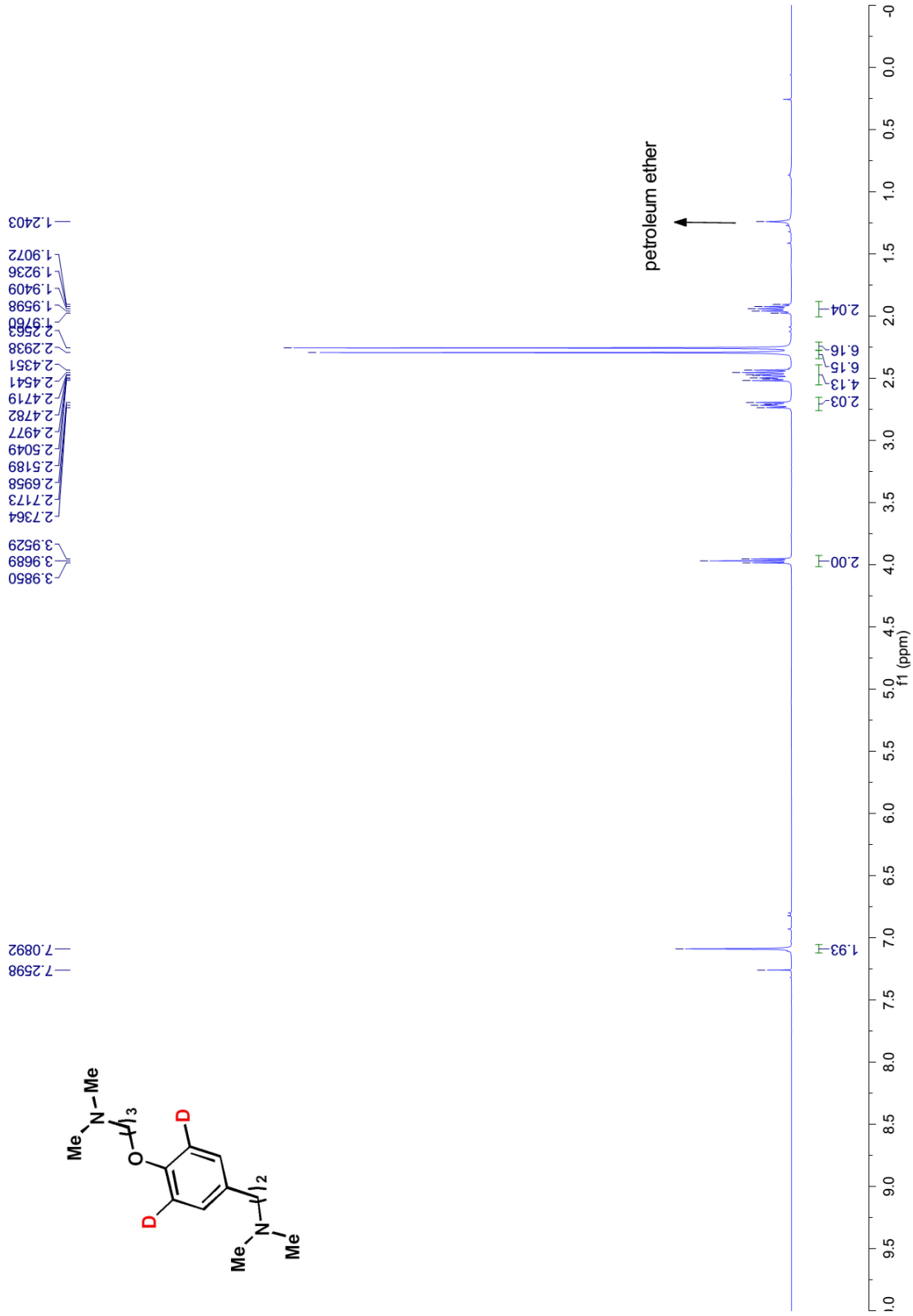

$^1$H NMR (400 MHz, $CDCl_3$) of ***7h***



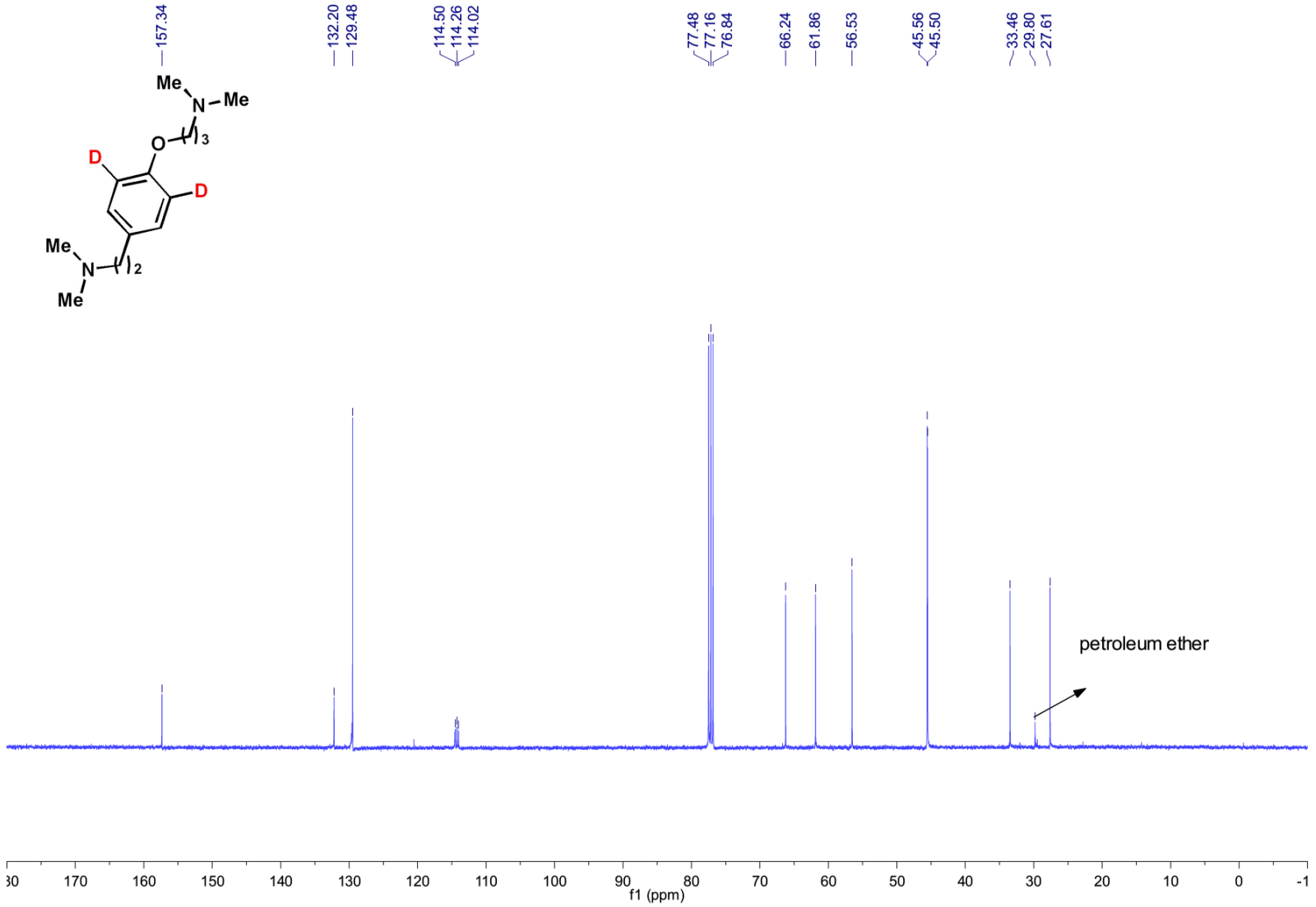

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***7h***



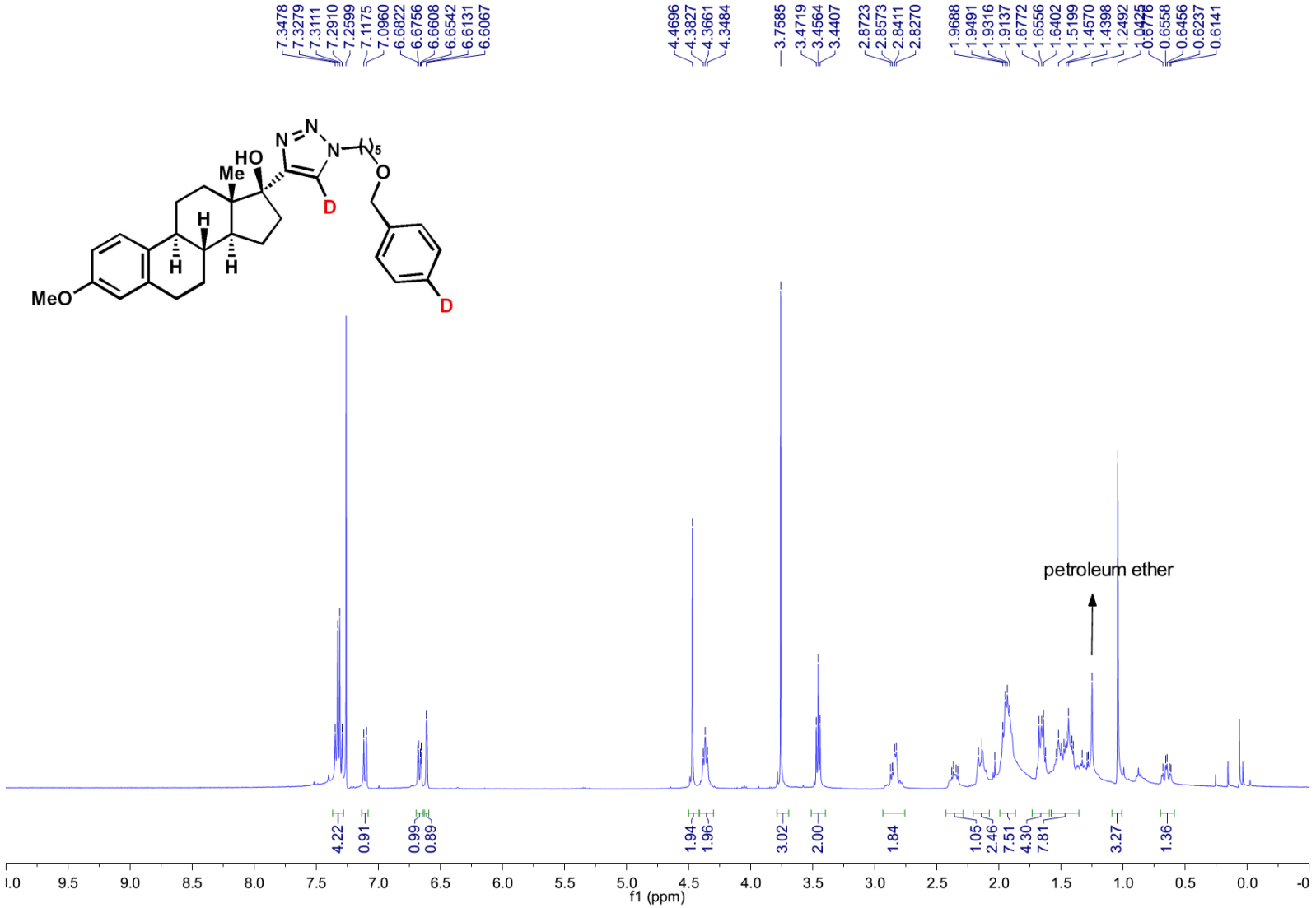

$^{2}$H NMR (122 MHz, $CHCl_3$) of ***7h***



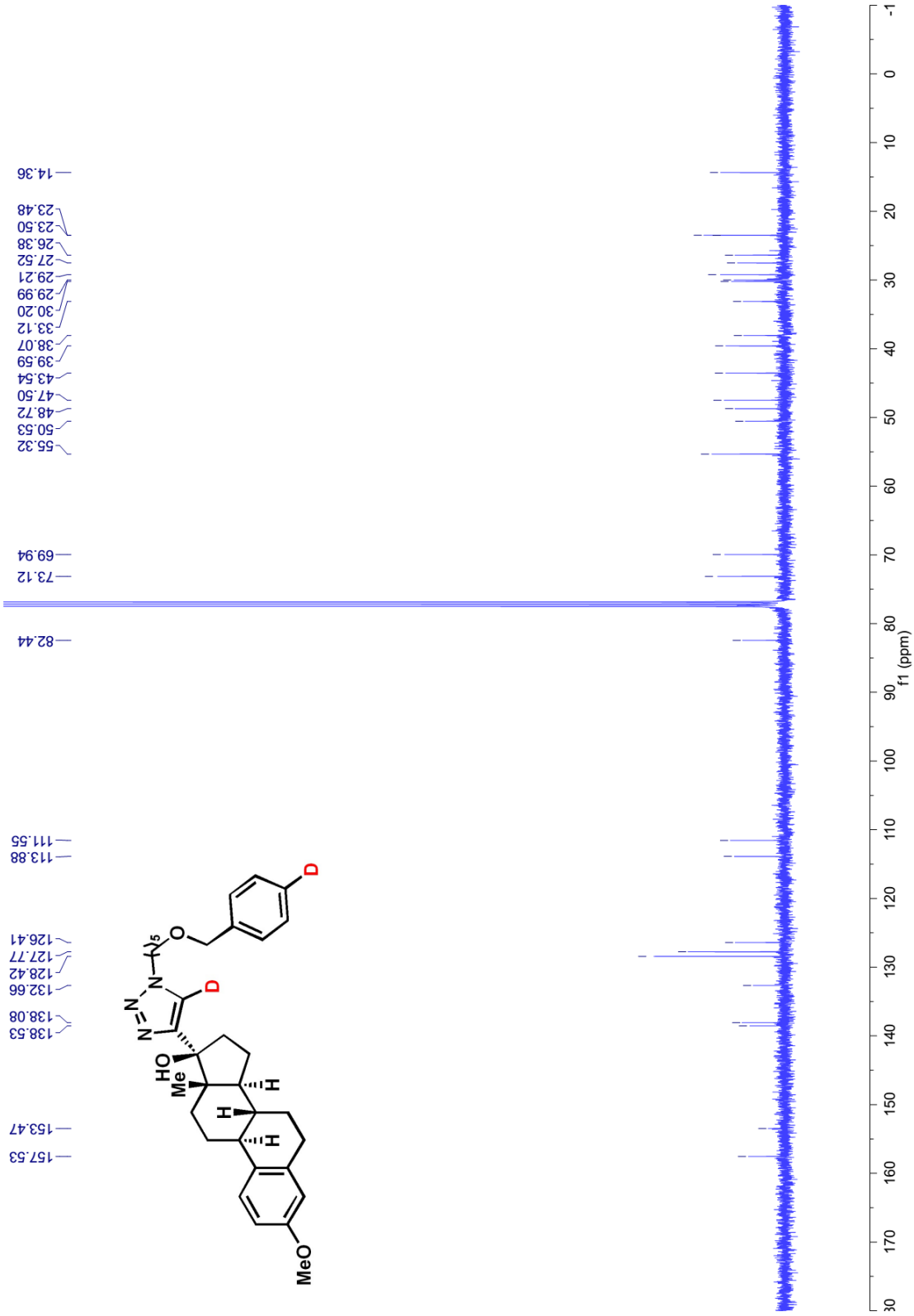

$^1$H NMR (400 MHz, $CDCl_3$) of ***7i***



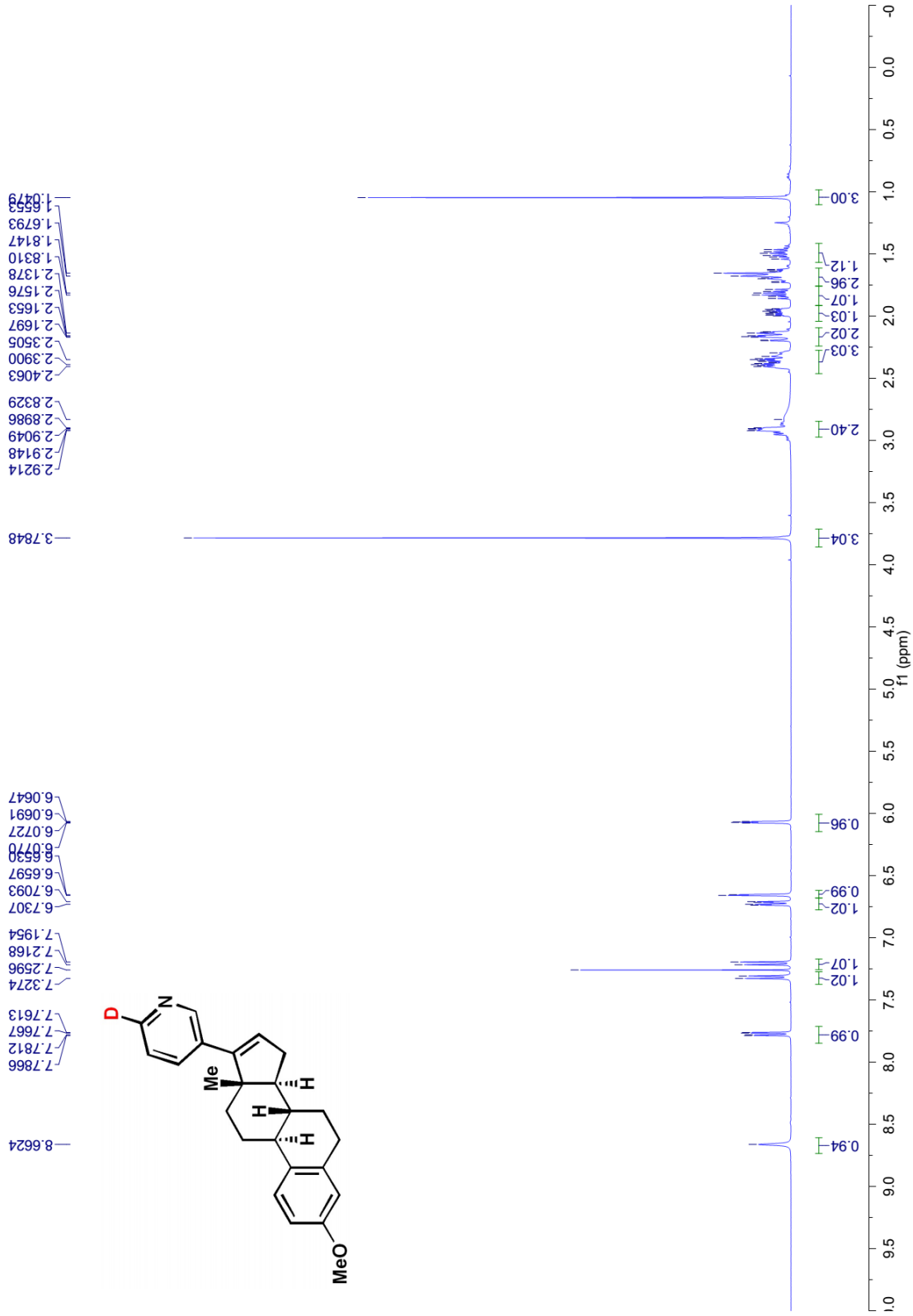

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***7i***



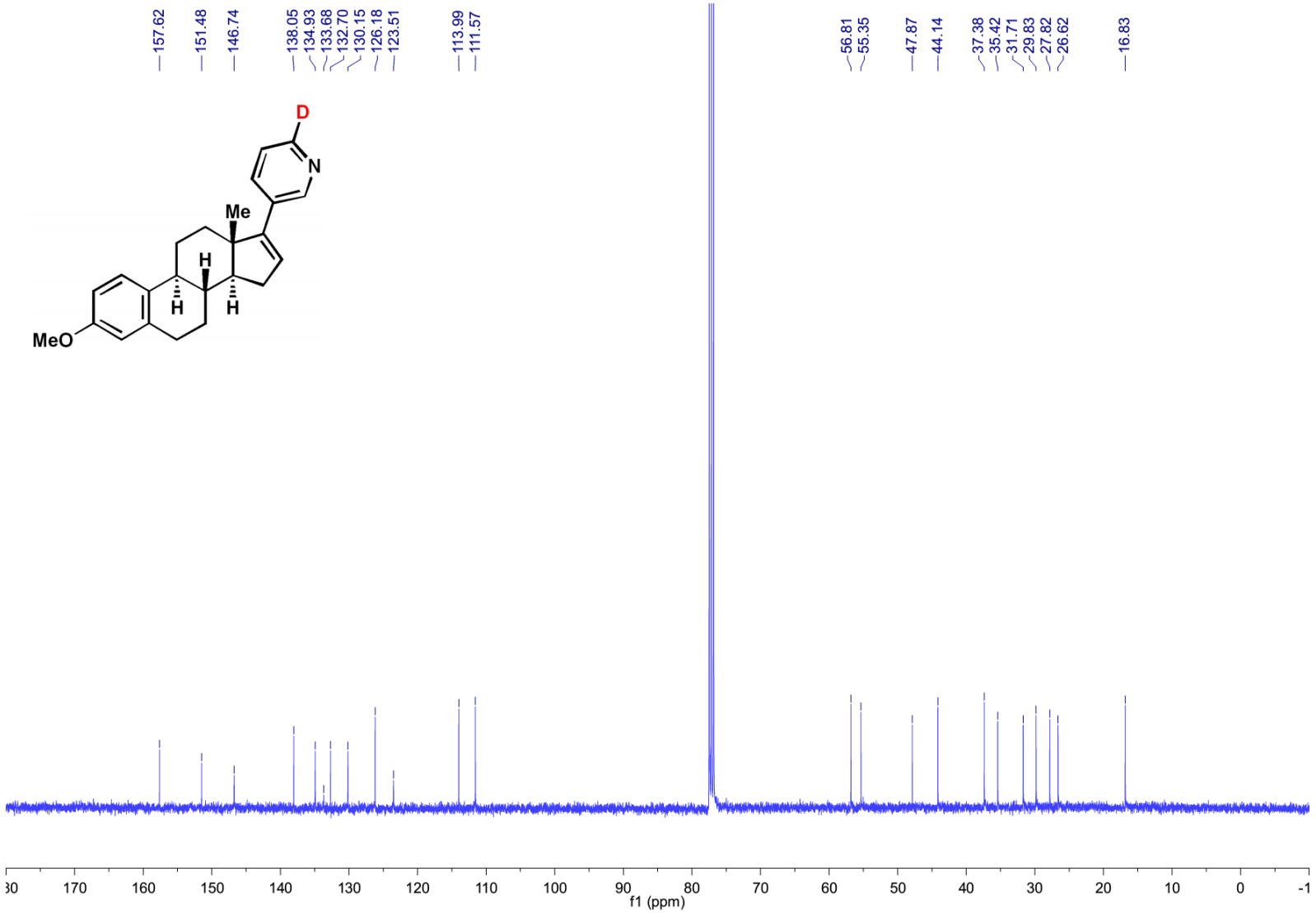

$^{1}$H NMR (400 MHz, $CDCl_3$) of ***7j***



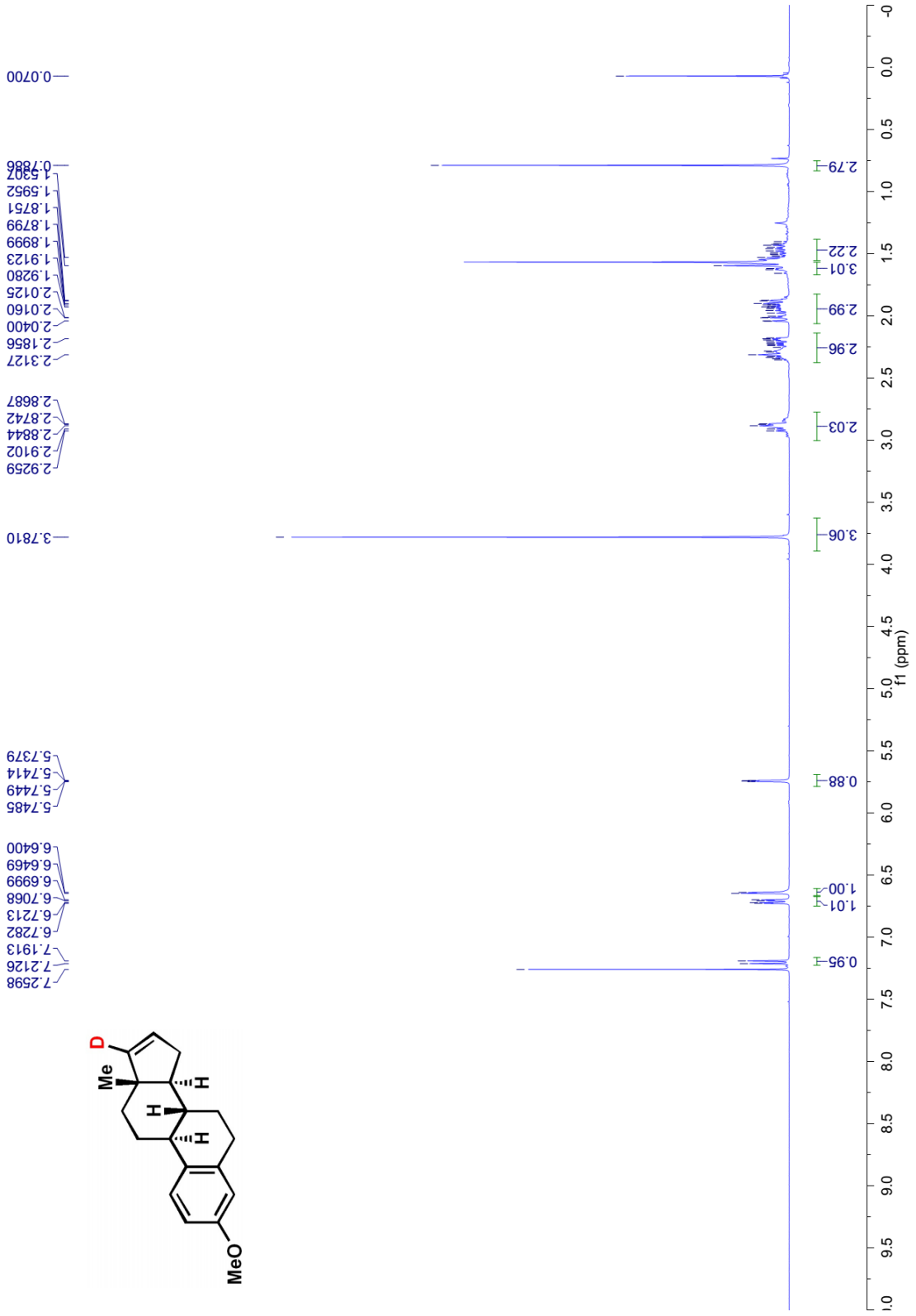

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***7j***



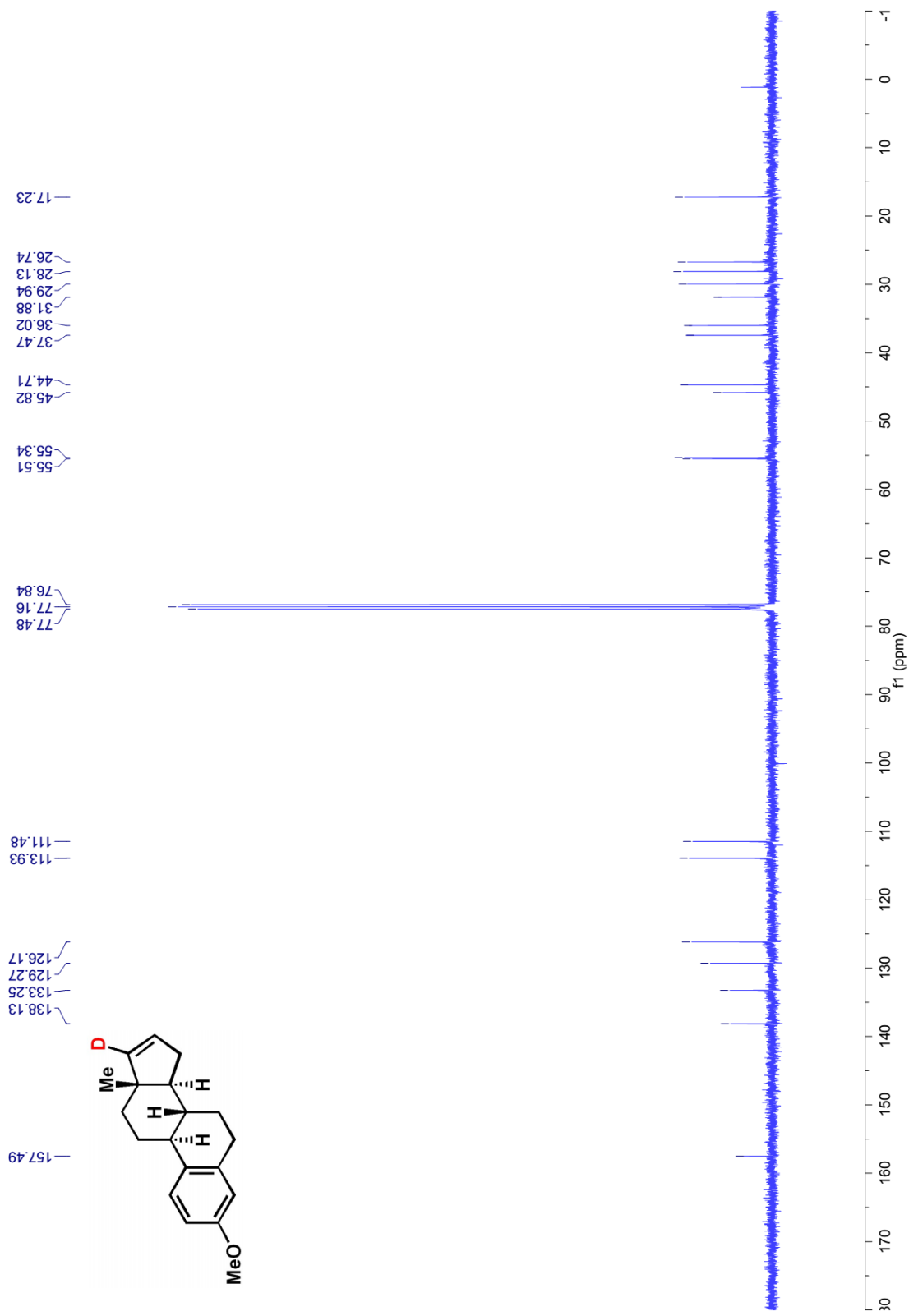

$^1$H NMR (400 MHz, $CDCl_3$) of ***7k***



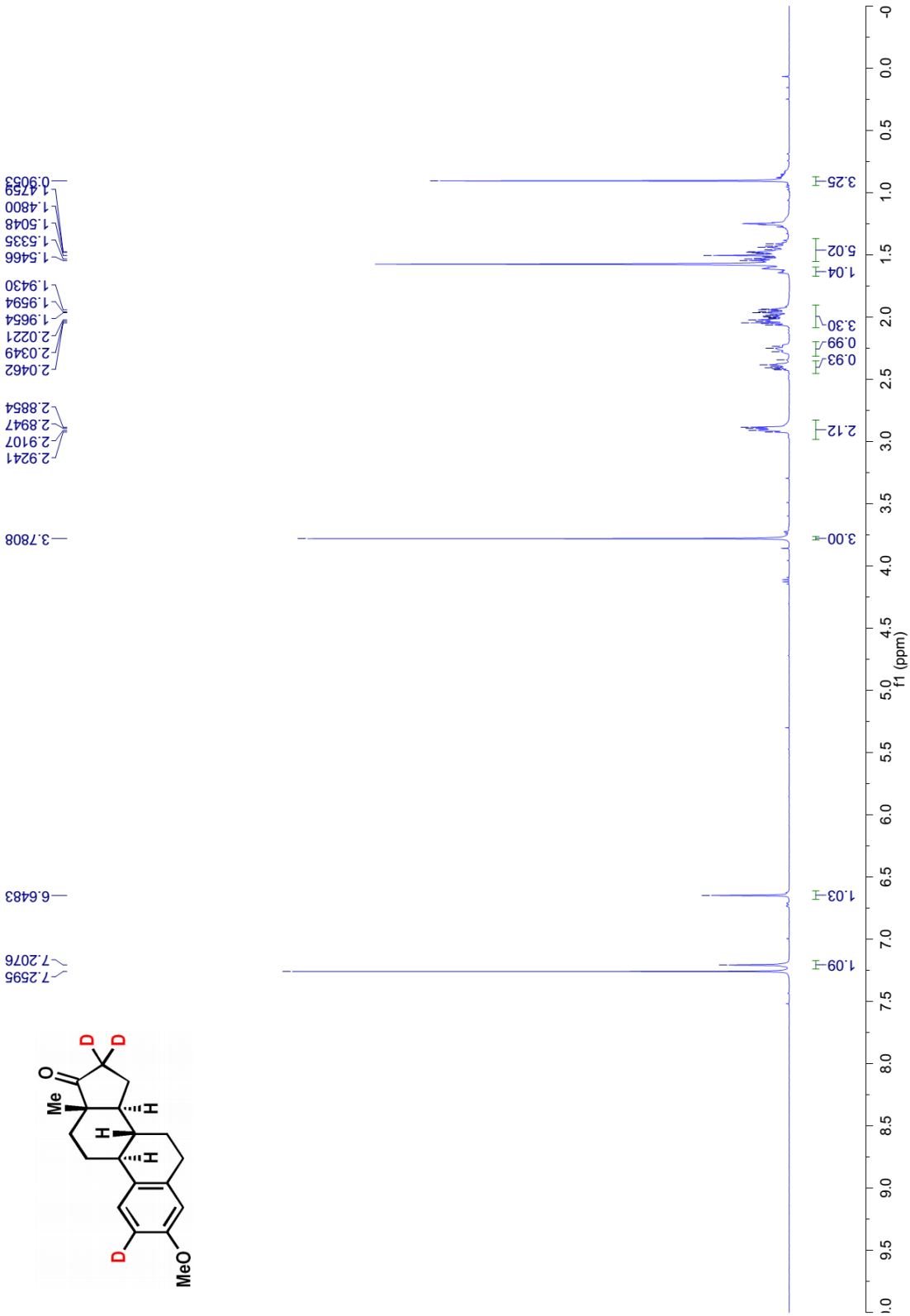

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***7k***



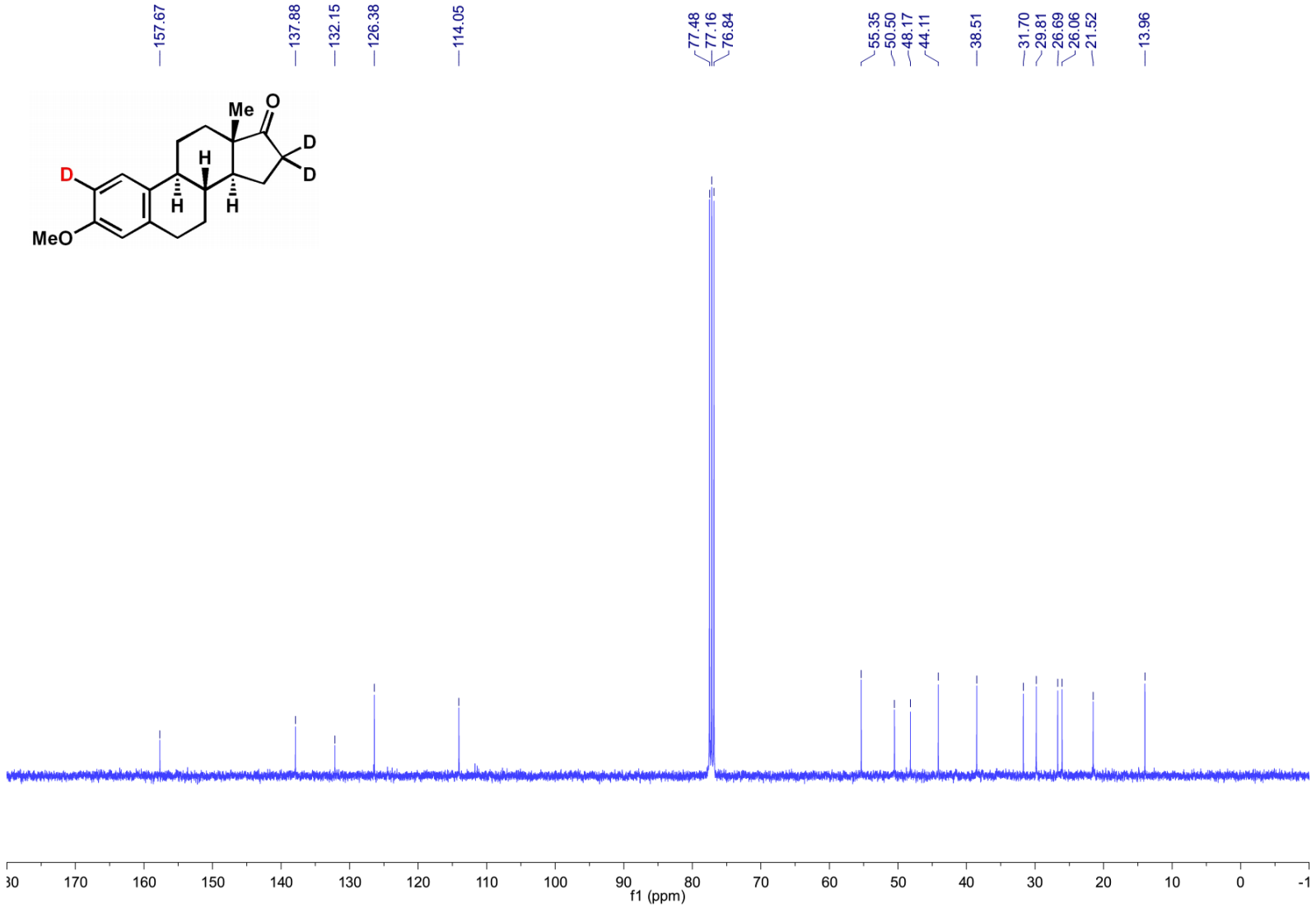

$^1$H NMR (400 MHz, $CDCl_3$) of ***7l***



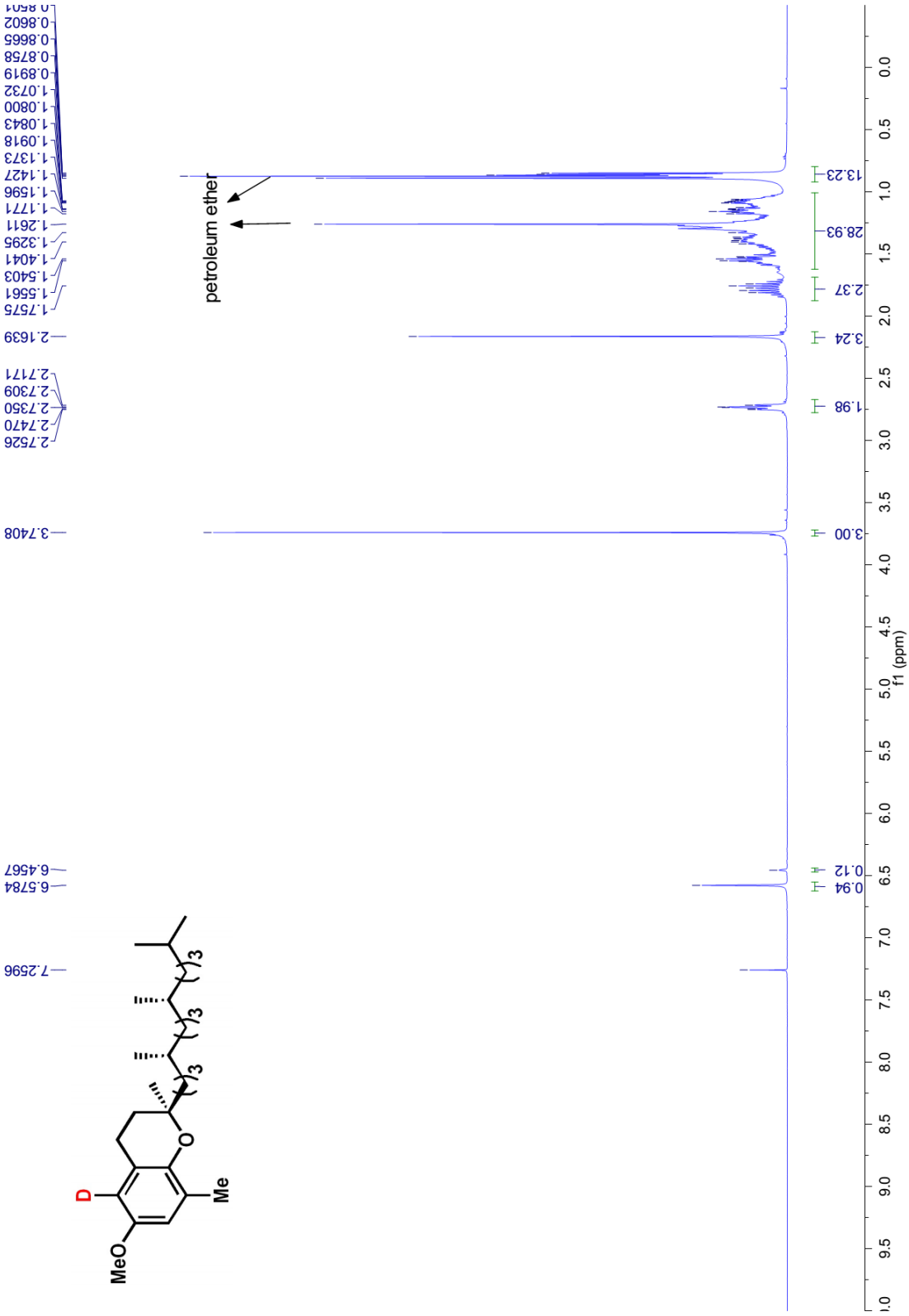

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***7l***



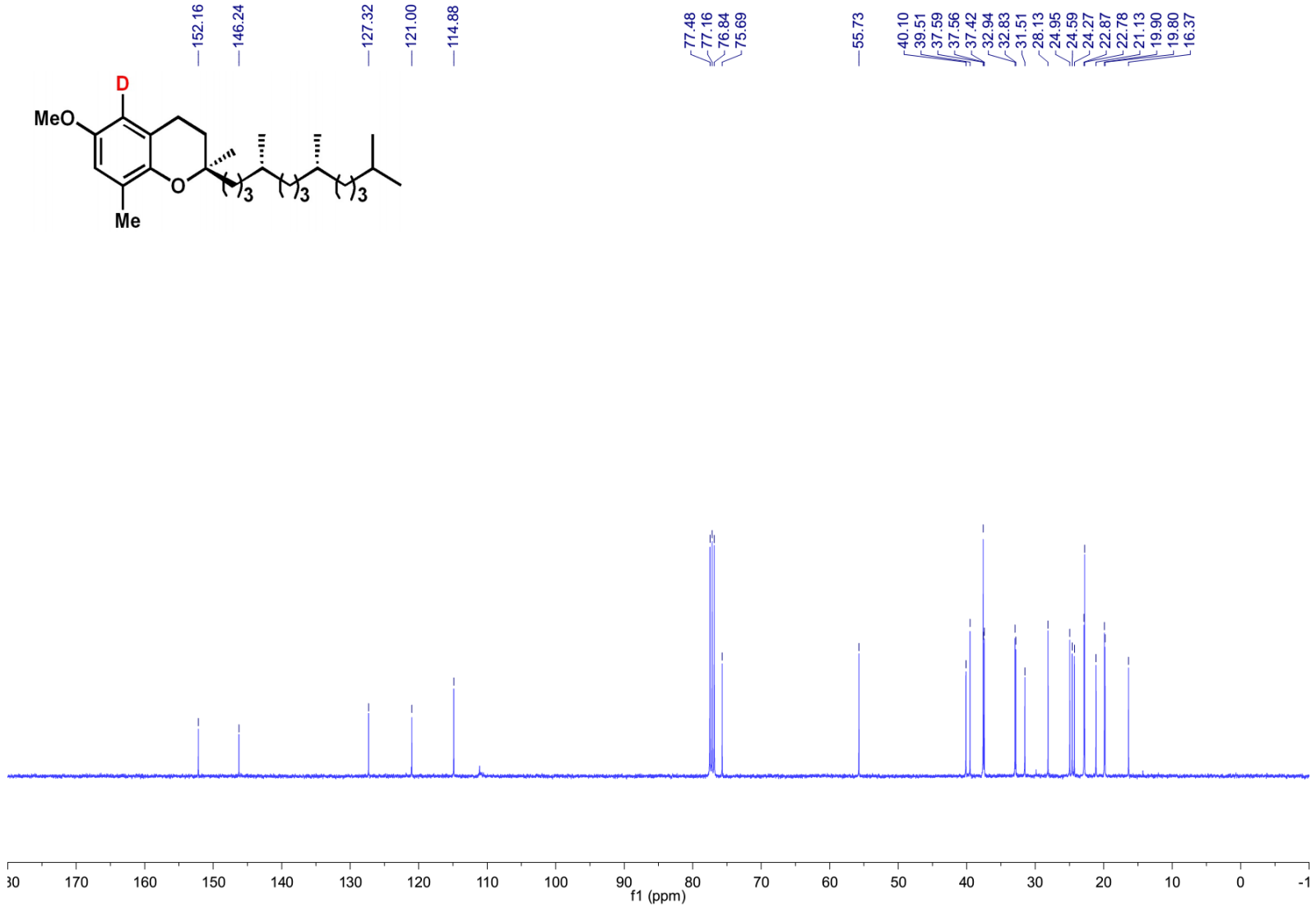

$^1$H NMR (400 MHz, $CDCl_3$) of ***7m***



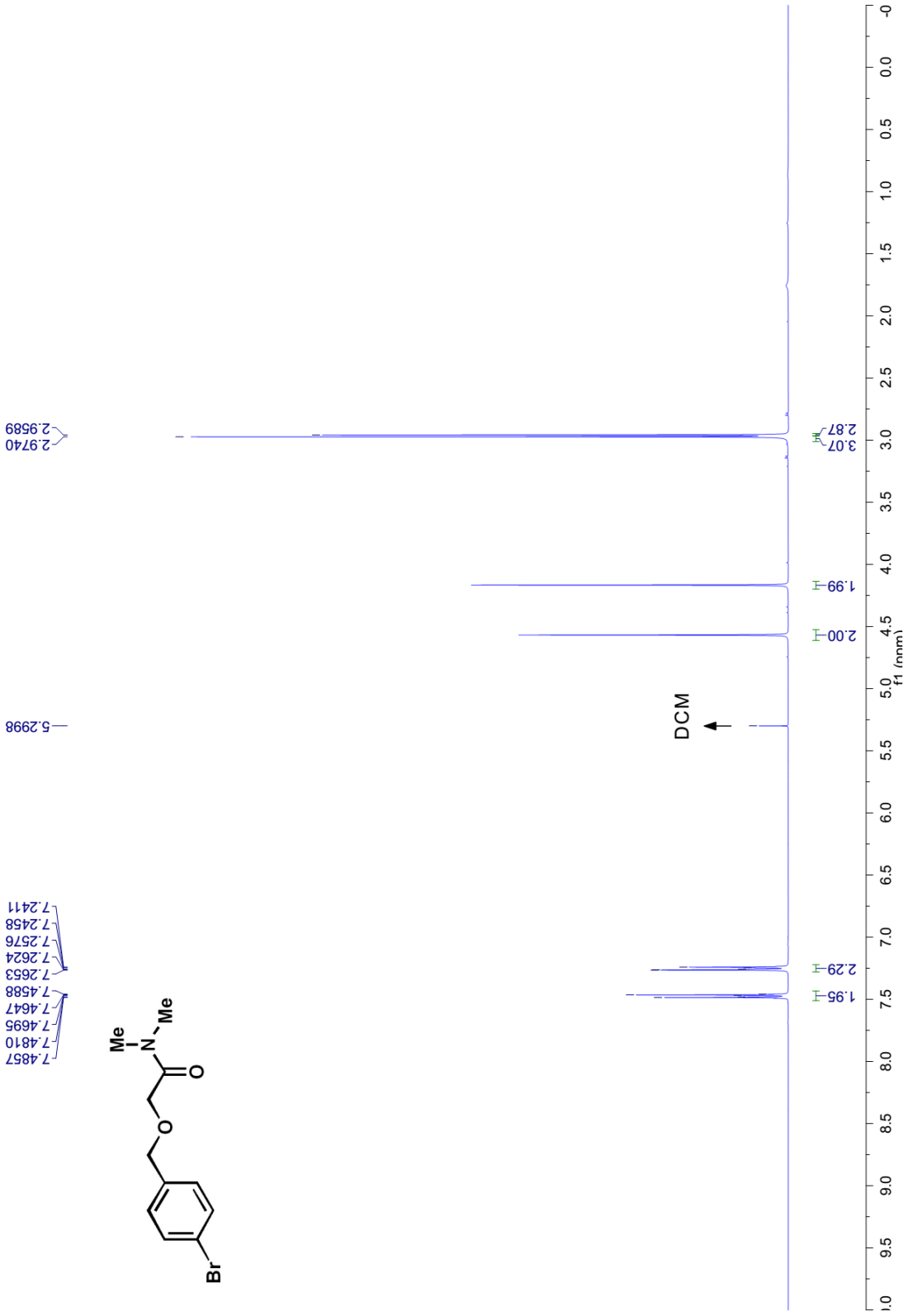

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***7m***



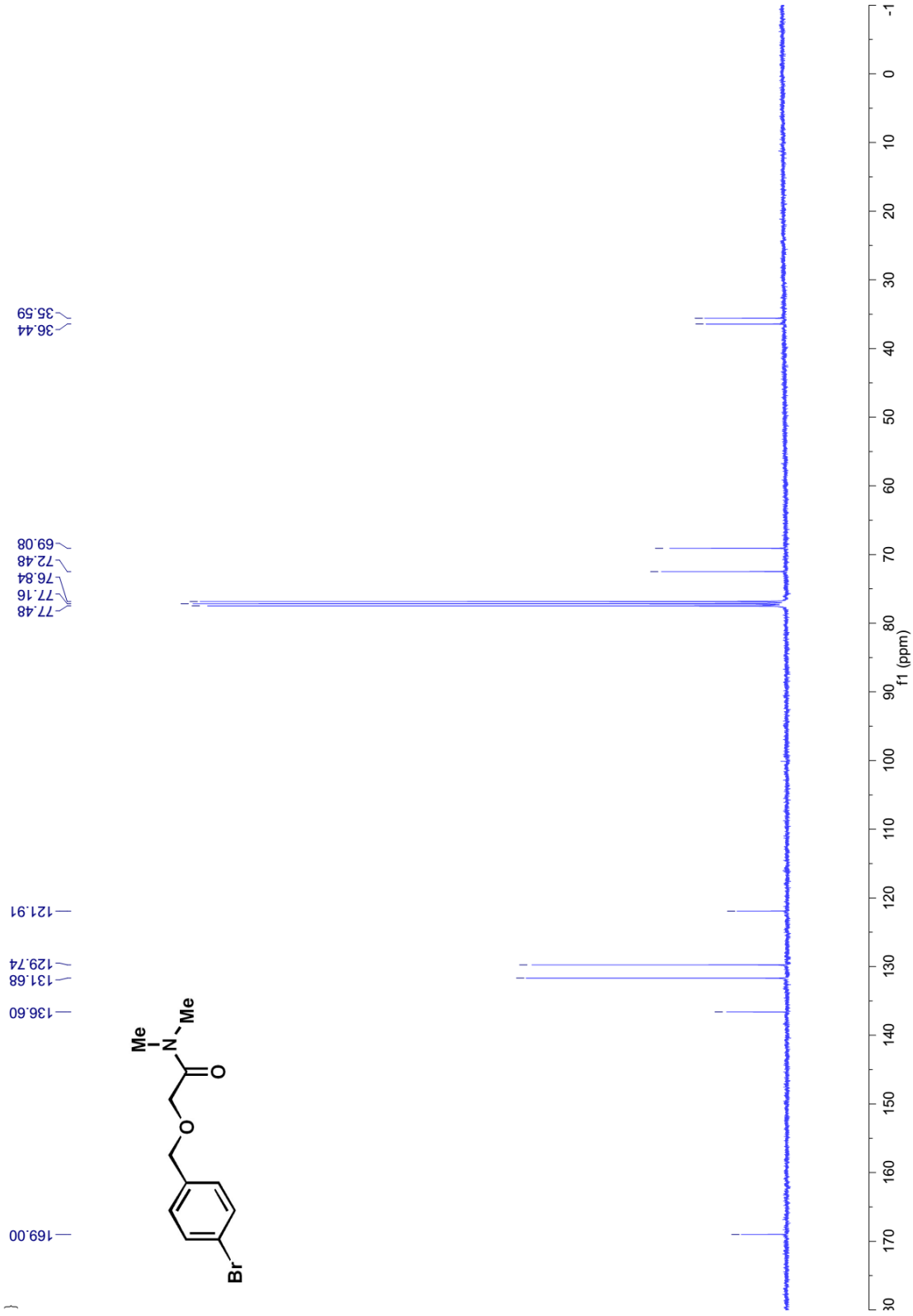

$^1$H NMR (400 MHz, $CDCl_3$) of ***7n***



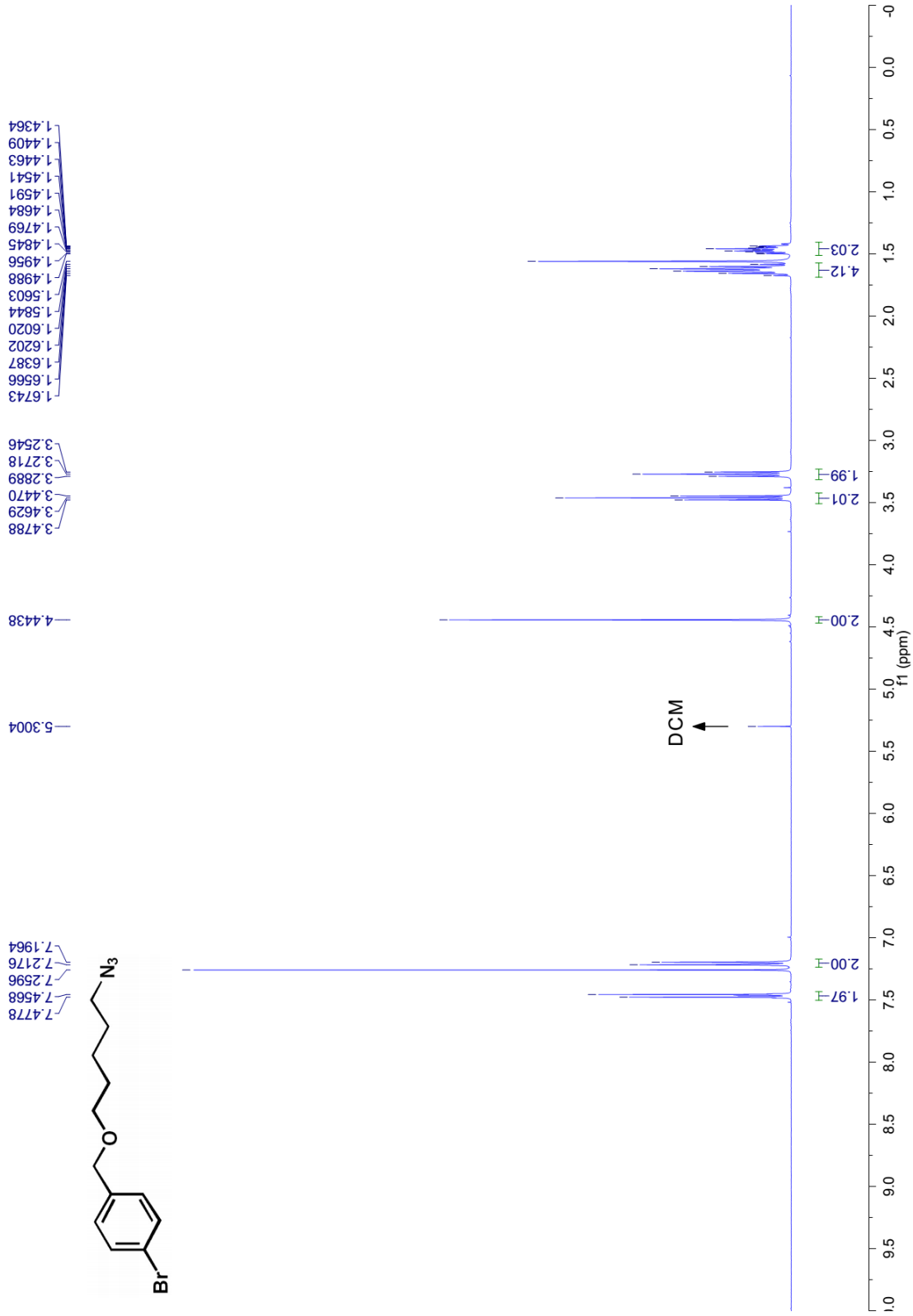

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***7n***



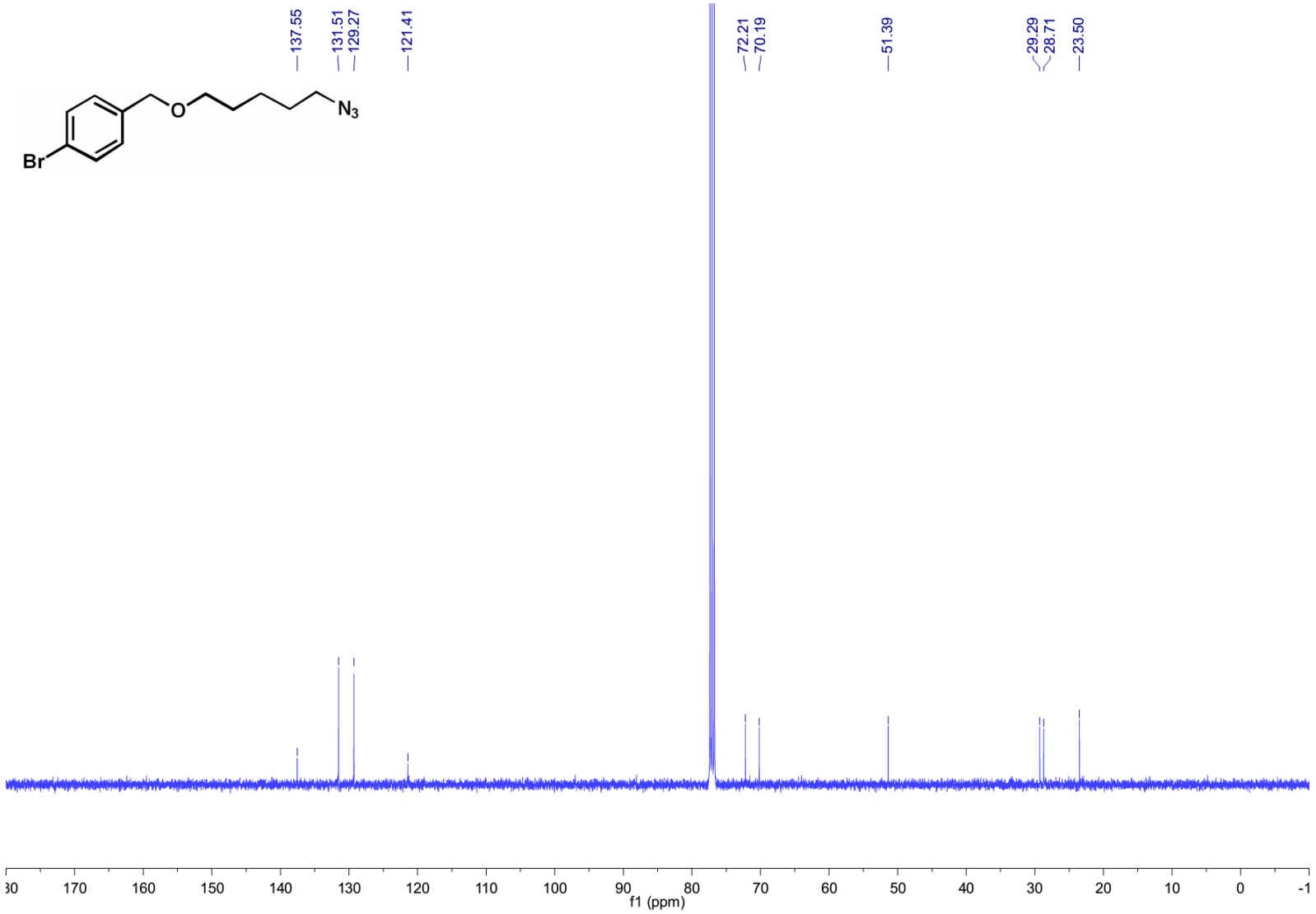

$^1$H NMR (400 MHz, $CDCl_3$) of ***S5a***



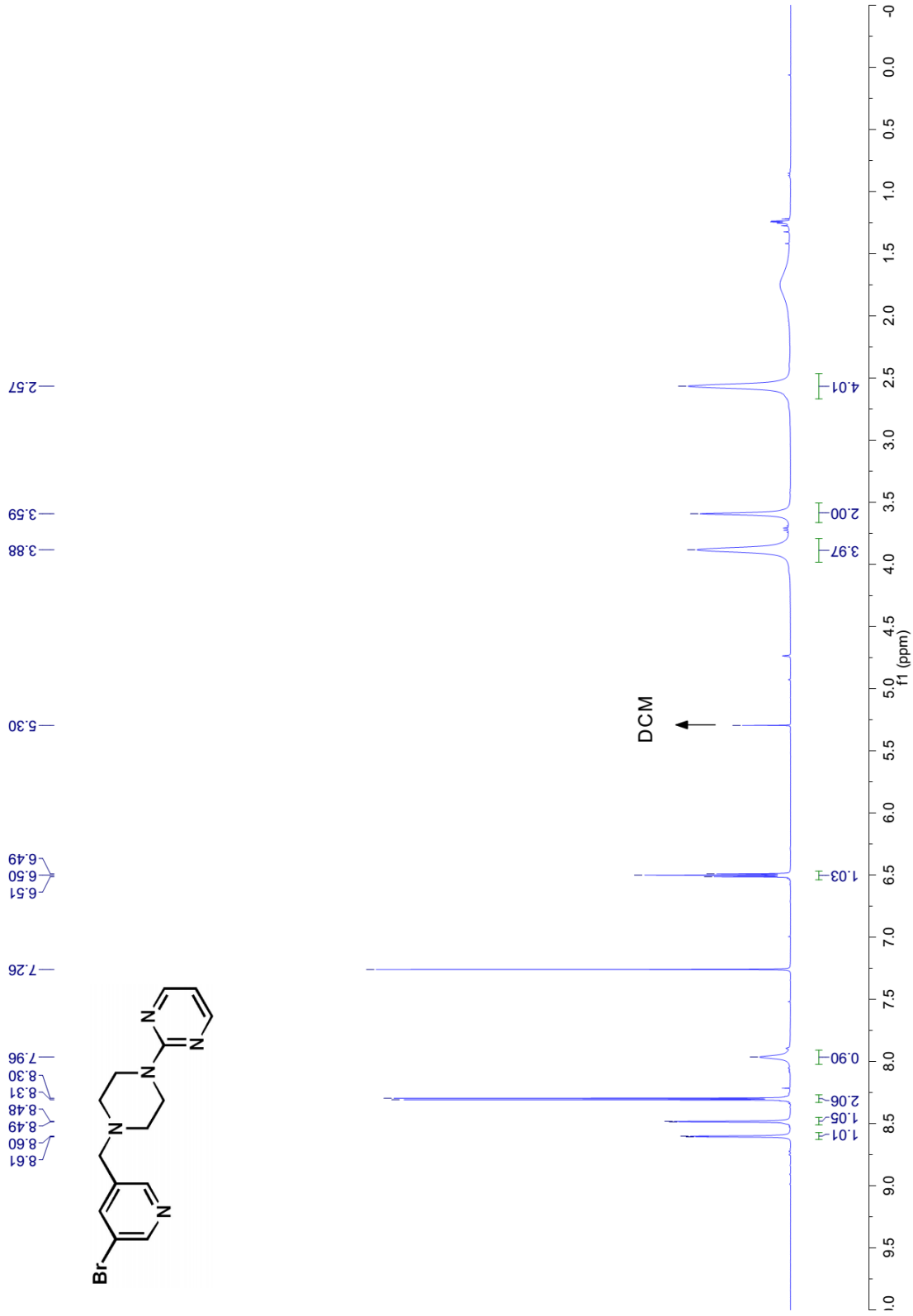

$^{13}$C NMR (100 MHz,, $CDCl_3$) of ***S5a***



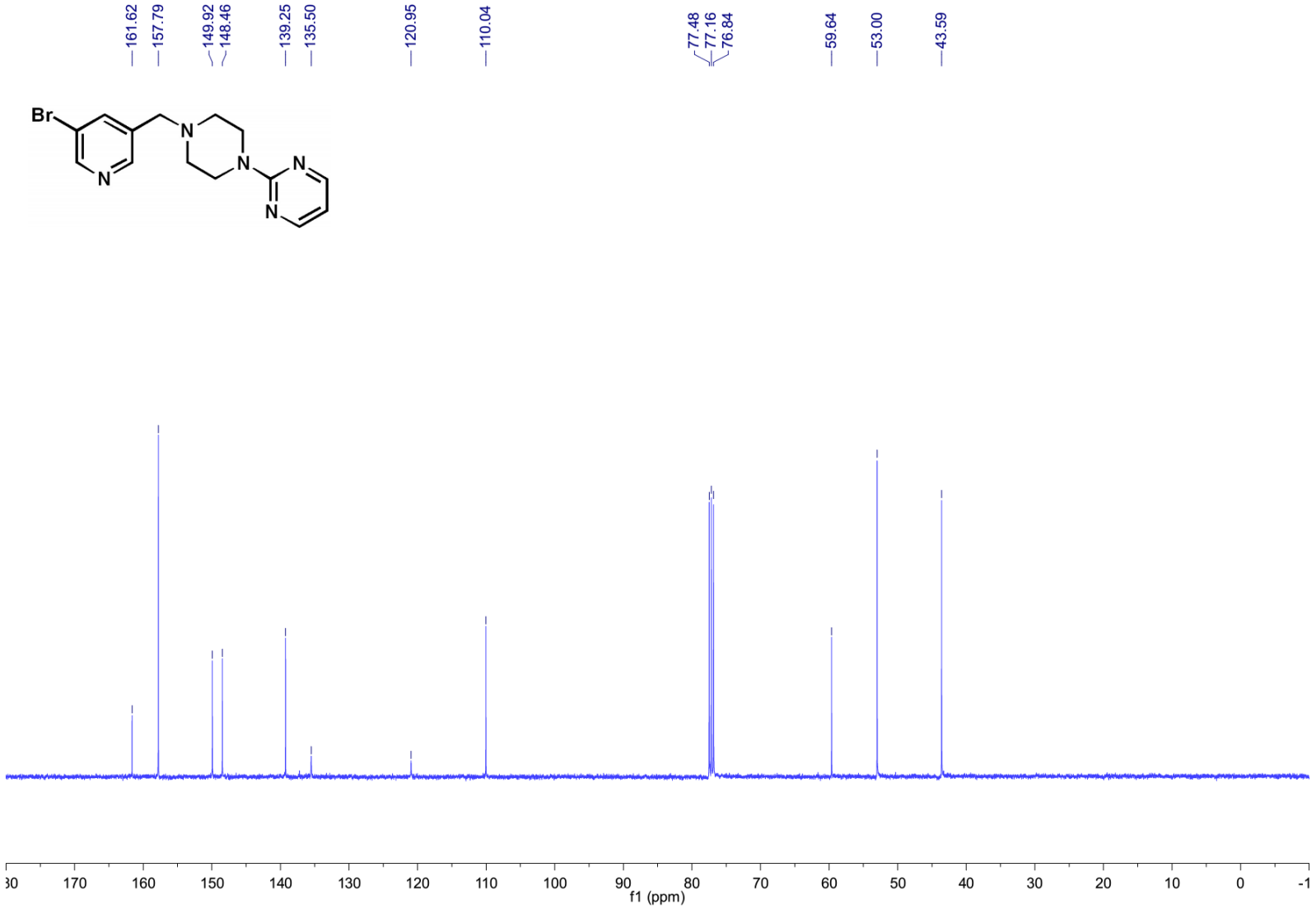

$^1$H NMR (400 MHz, $CDCl_3$) of ***S5d***



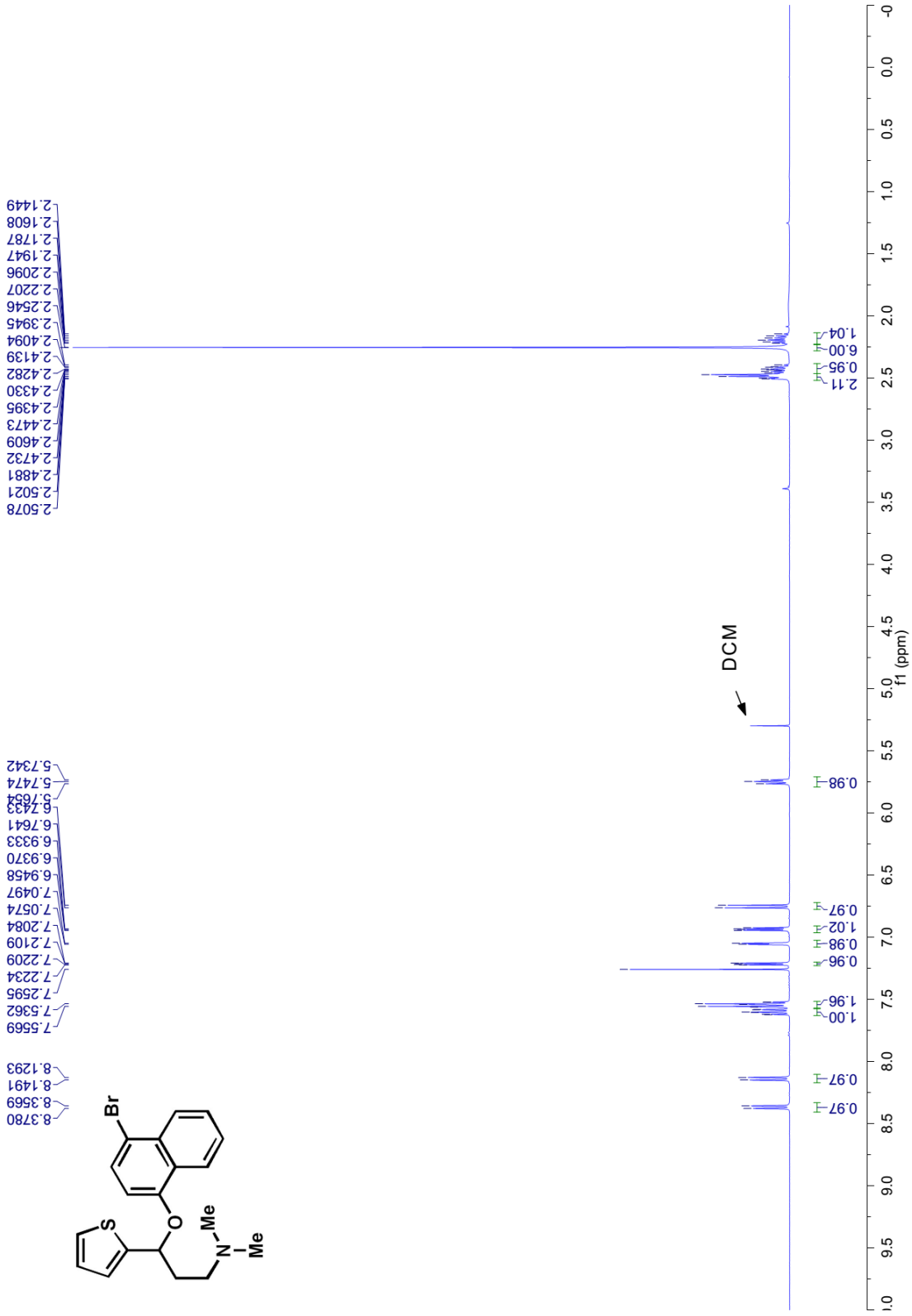

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***S5d***



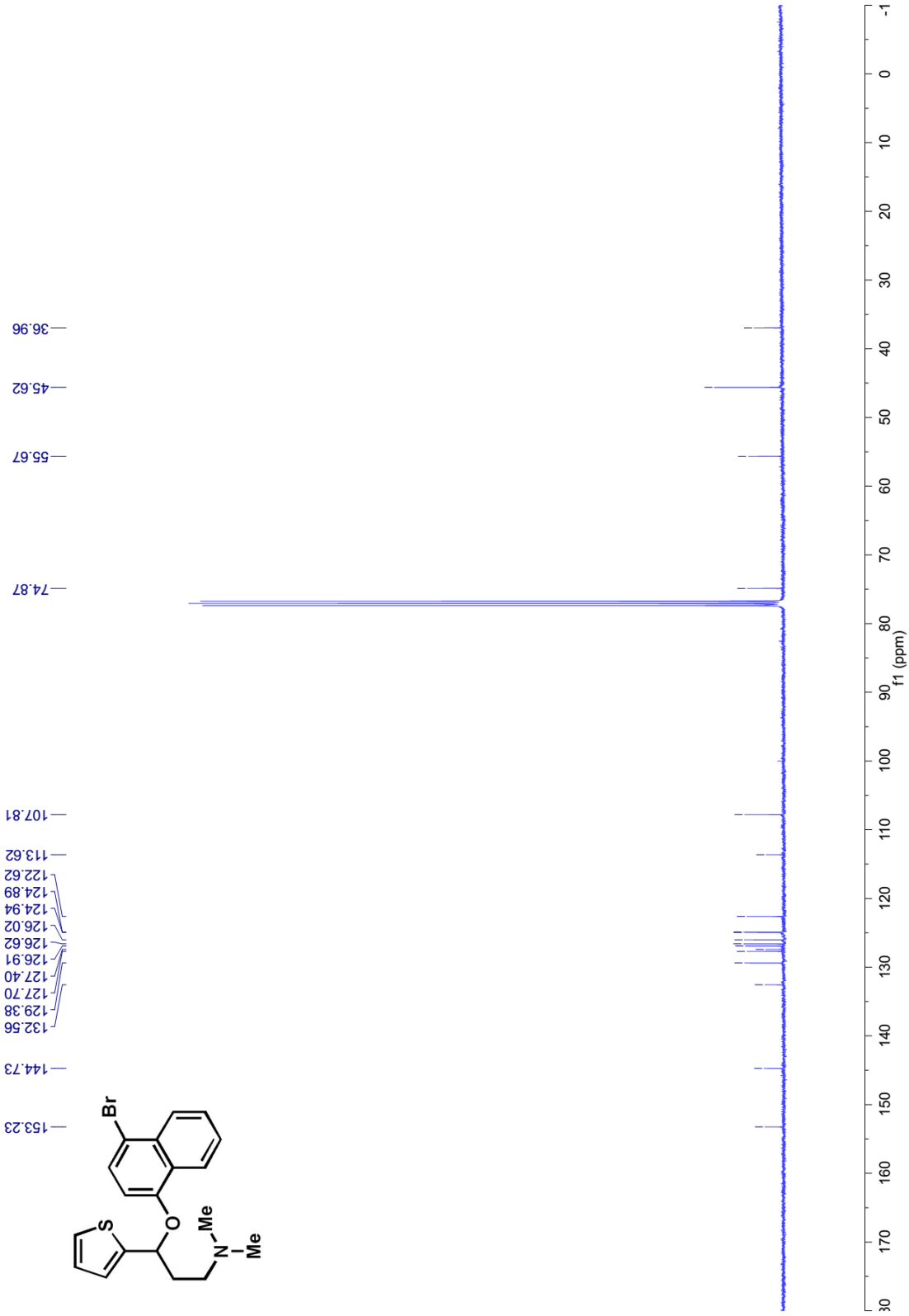

$^1$H NMR (400 MHz, $CDCl_3$) of ***S6c***




$^{13}$C NMR (100 MHz, $CDCl_3$) of ***S6c***

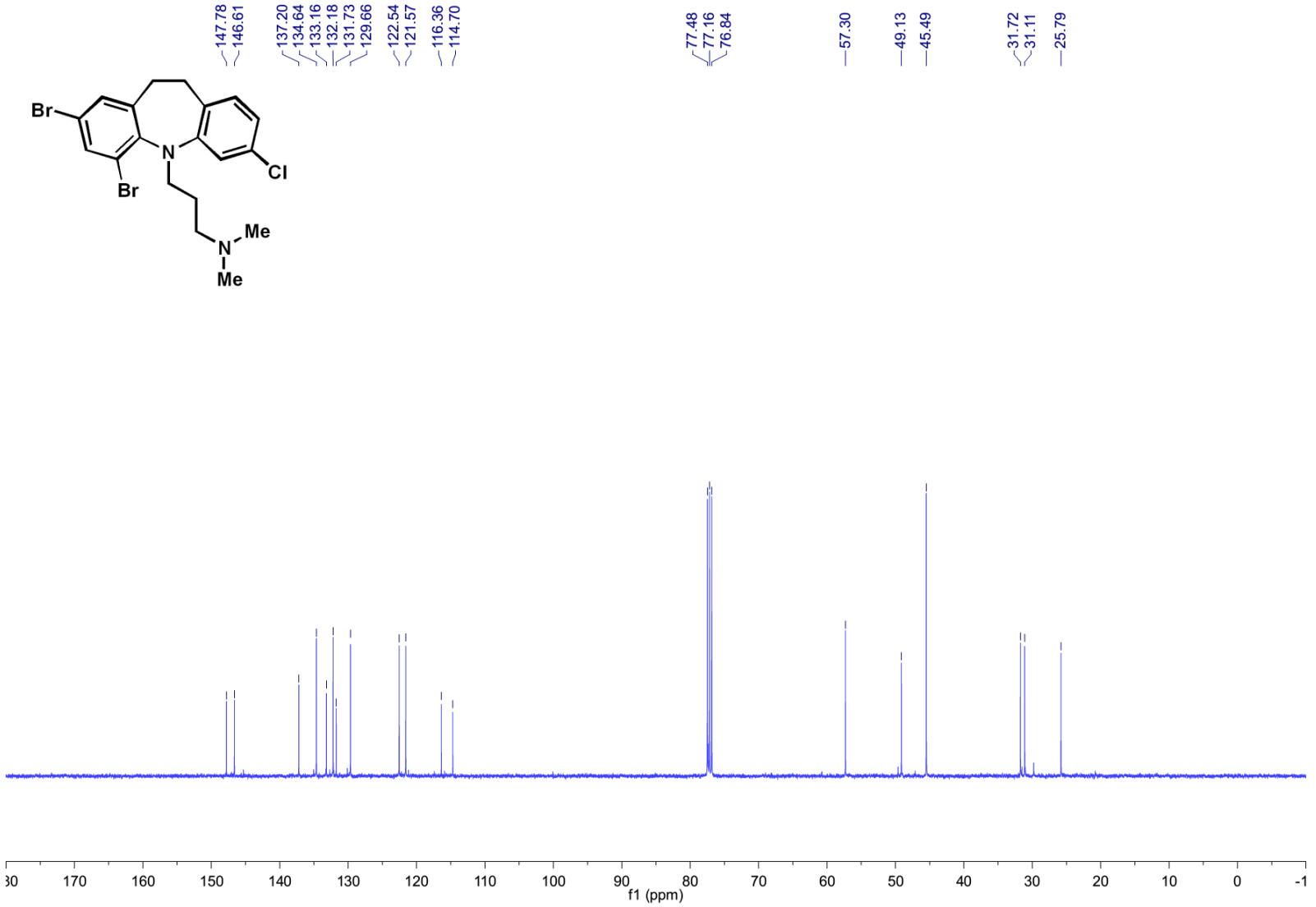



$^1$H NMR (400 MHz, $CDCl_3$) of ***S7e***

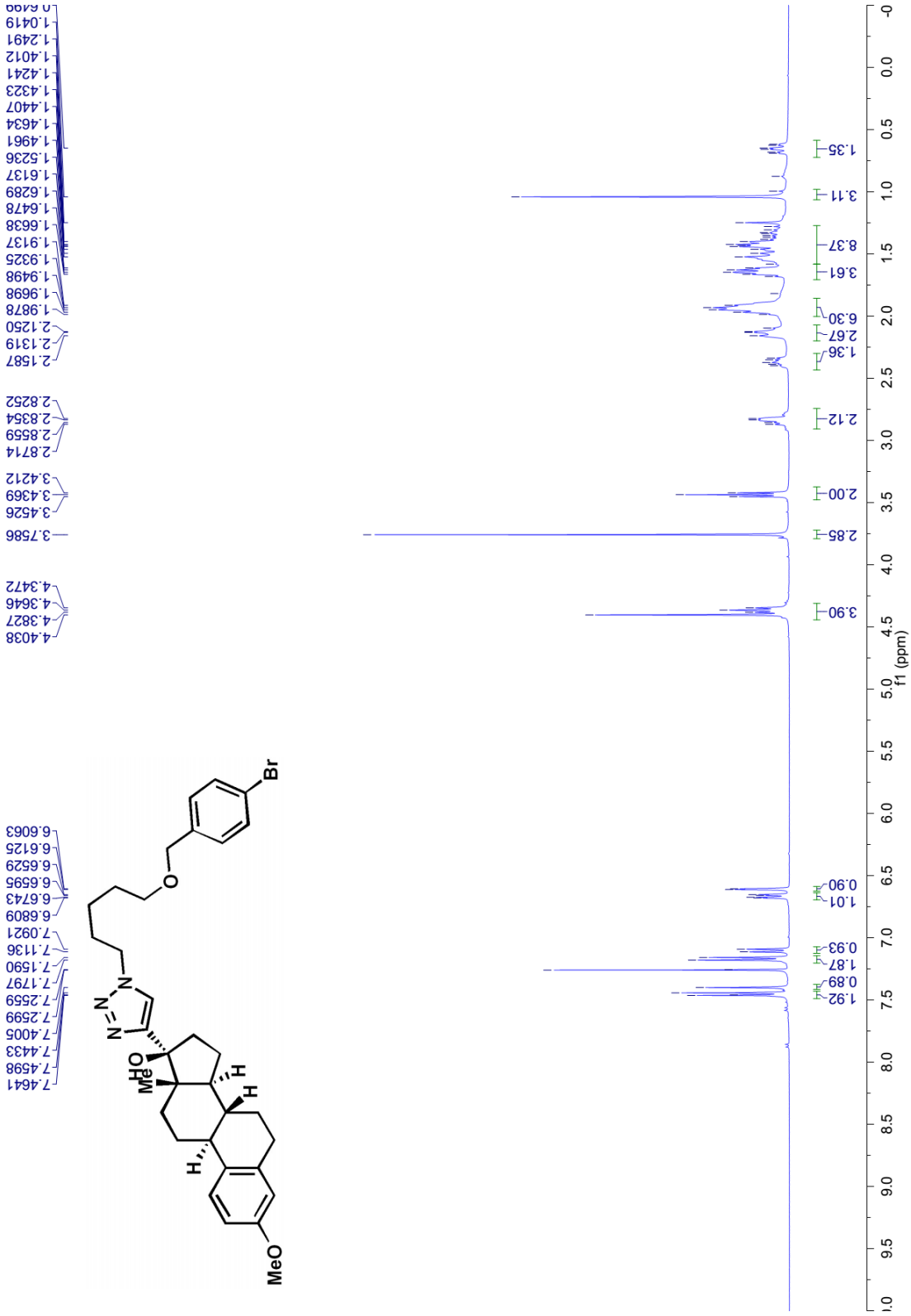



$^{13}$C NMR (100 MHz, $CDCl_3$) of ***S7e***

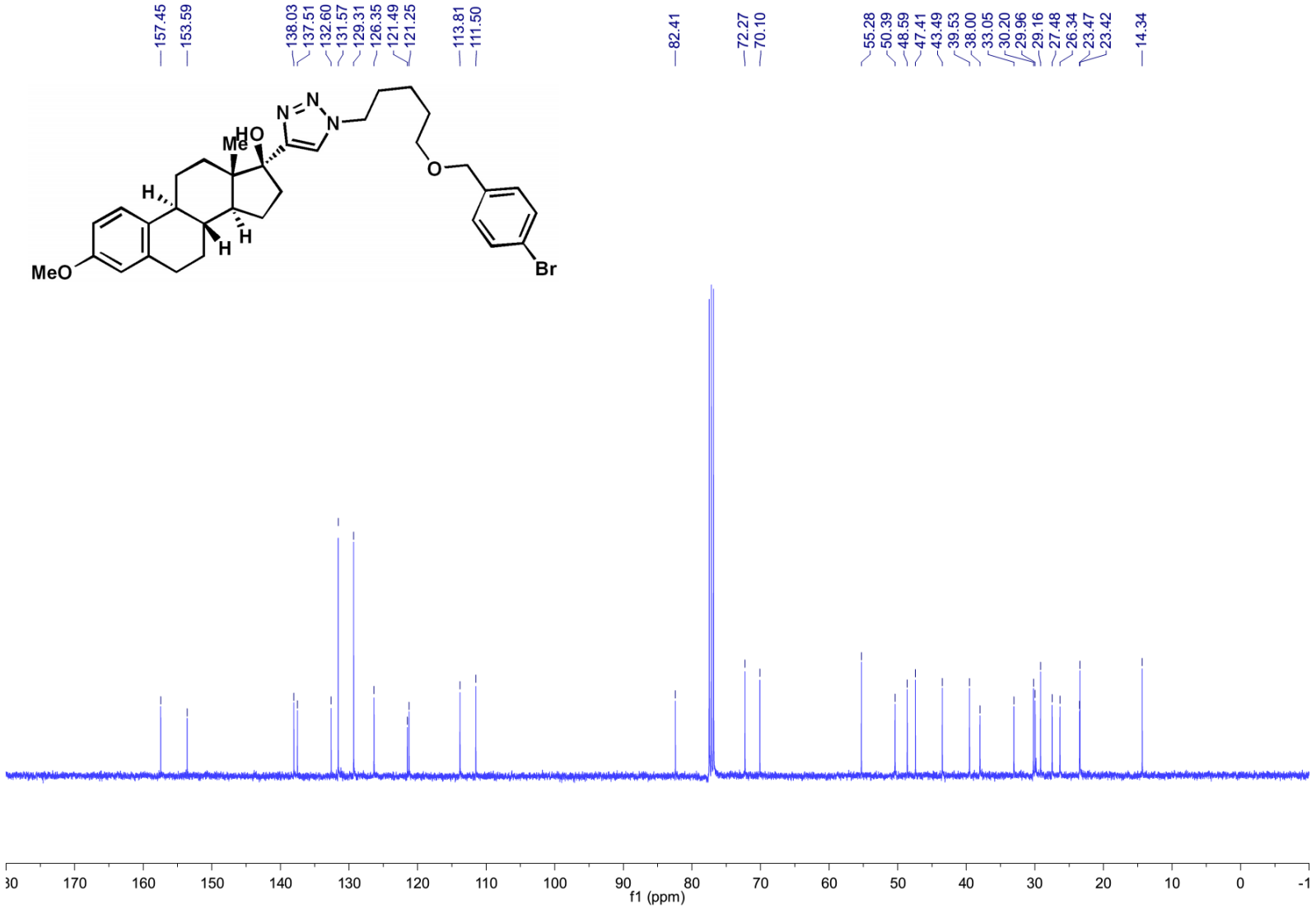

$^1$H NMR (400 MHz, $CDCl_3$) of ***S7h***



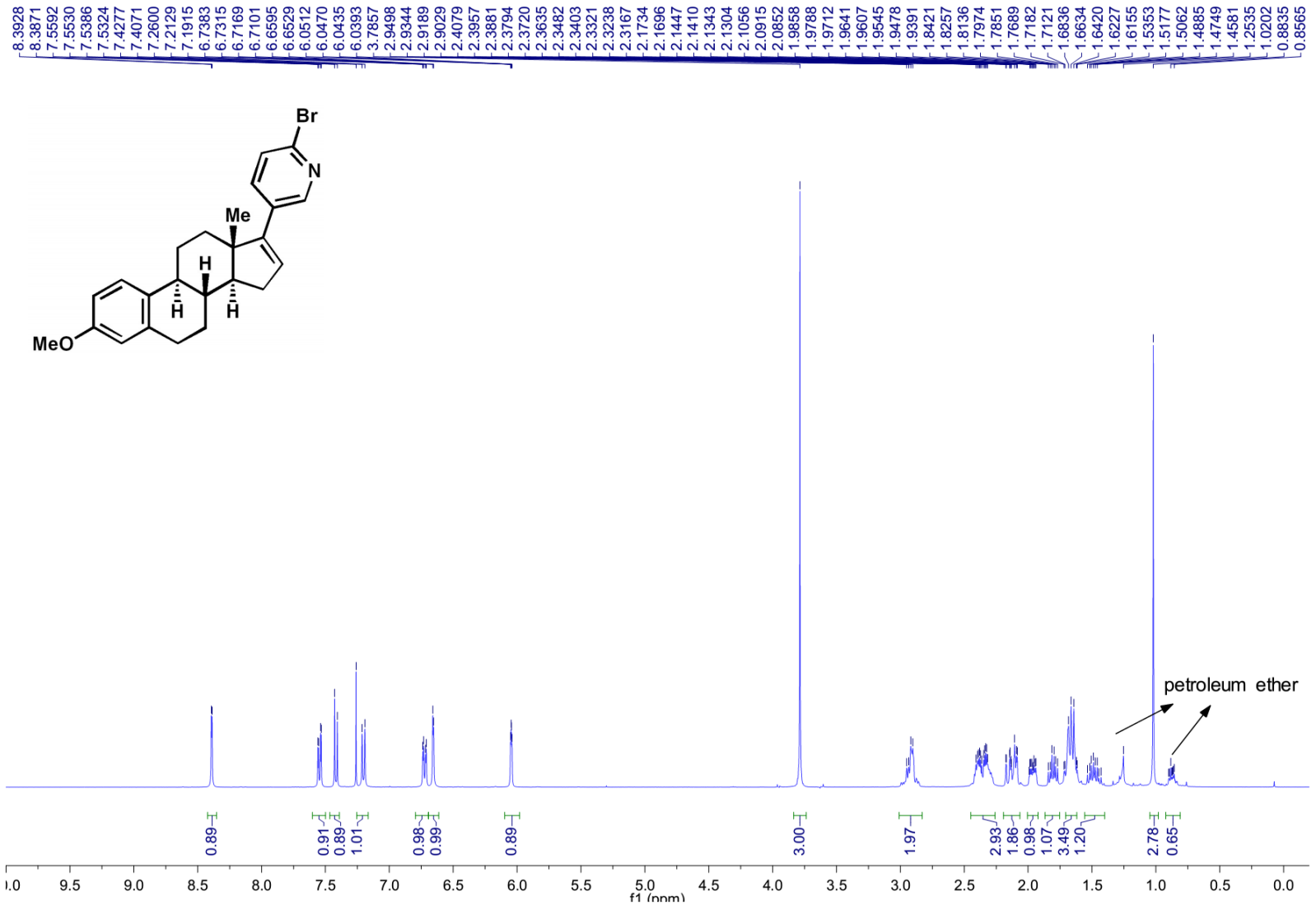

$^{13}$C NMR (100 MHz, $CDCl_3$) of ***S7h***



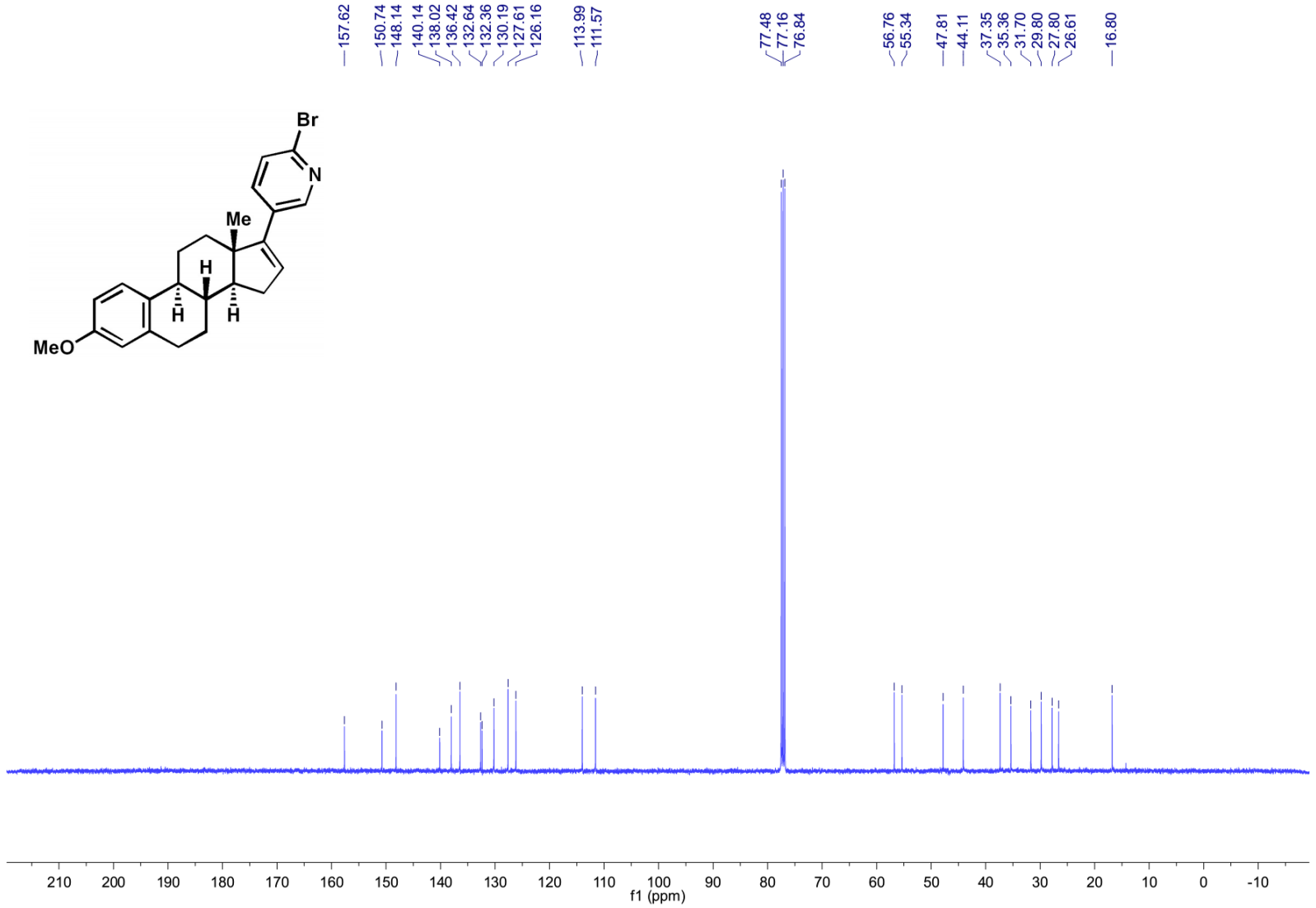

$^1$H NMR (400 MHz, $CDCl_3$) of ***S7i***




$^{13}$C NMR (100 MHz, $CDCl_3$) of ***S7i***

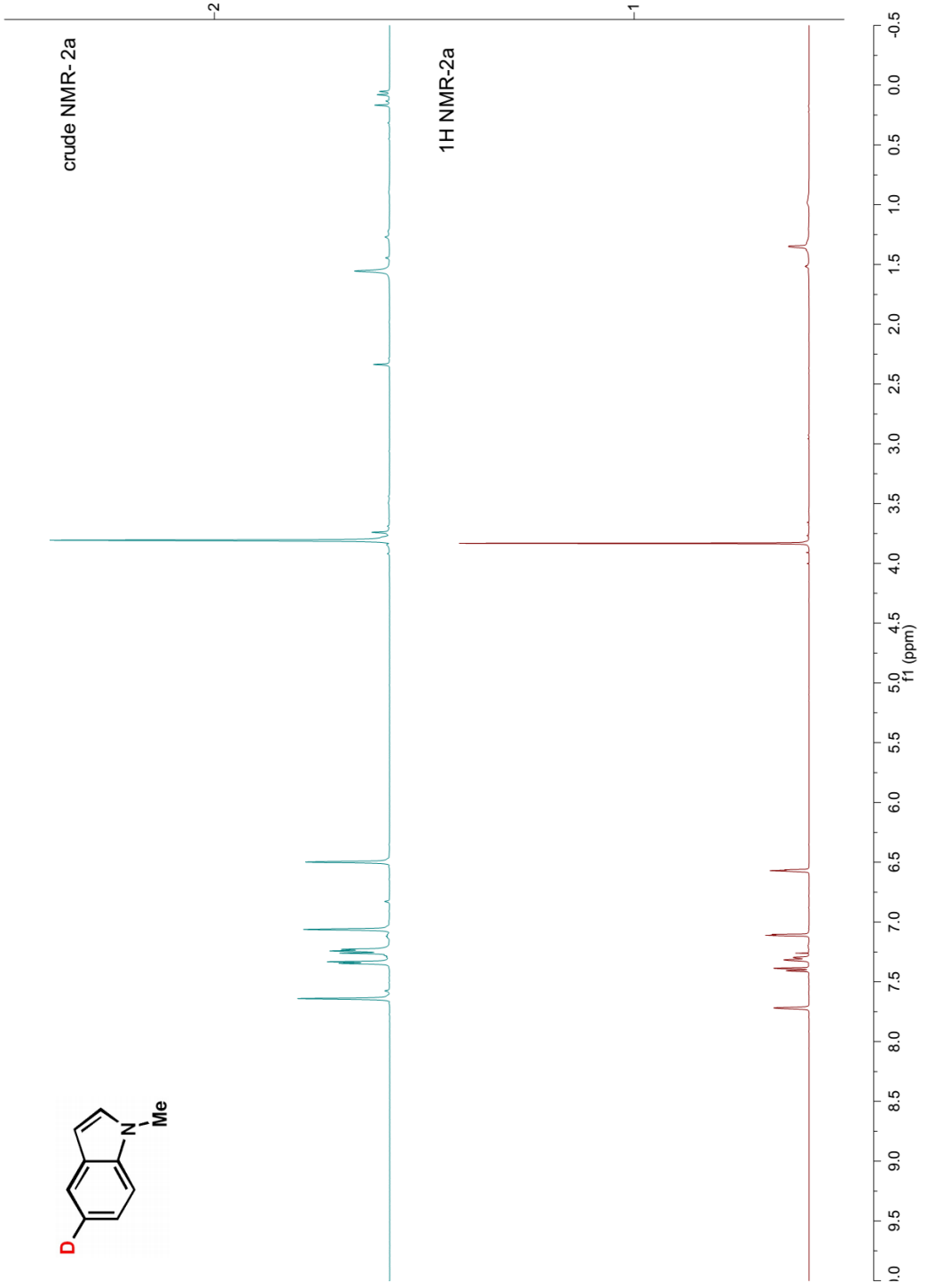


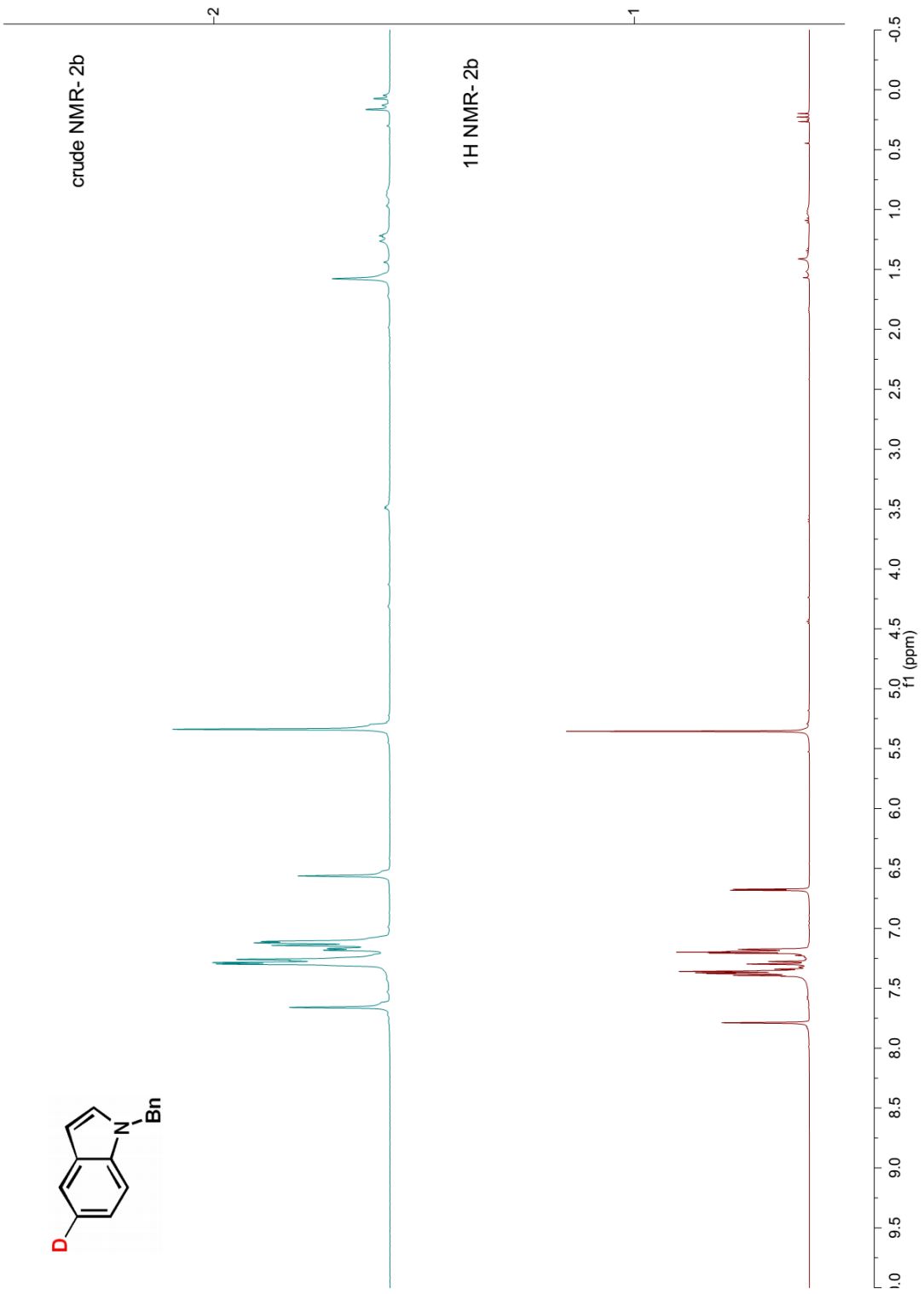

$^{1}$H NMR (400 MHz, $CDCl_3$) of ***S7k***




$^{13}$C NMR (100 MHz, $CDCl_3$) of ***S7k***

## Crude NMR Spectra for Dehalogenative Deuteration Reactions

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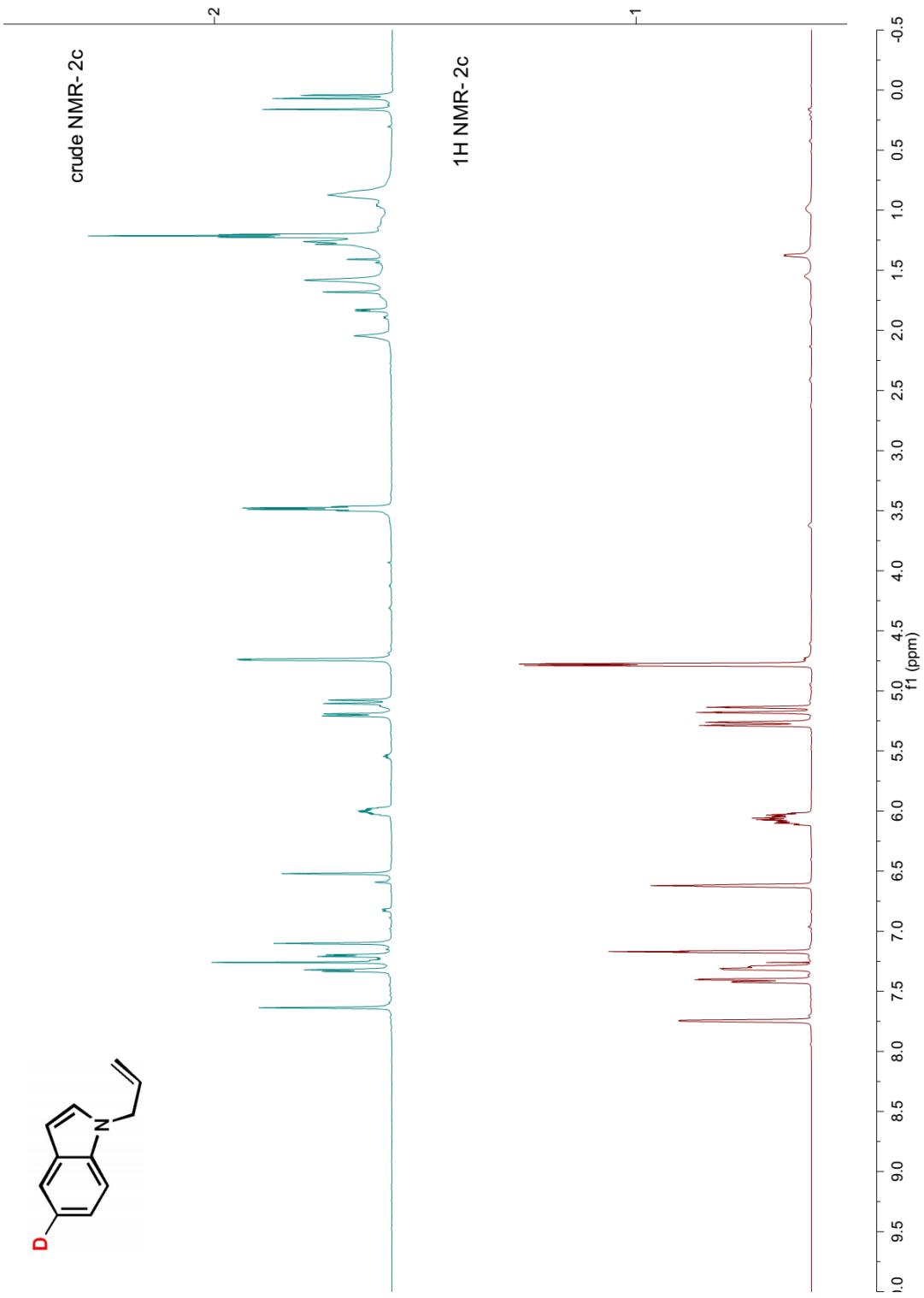
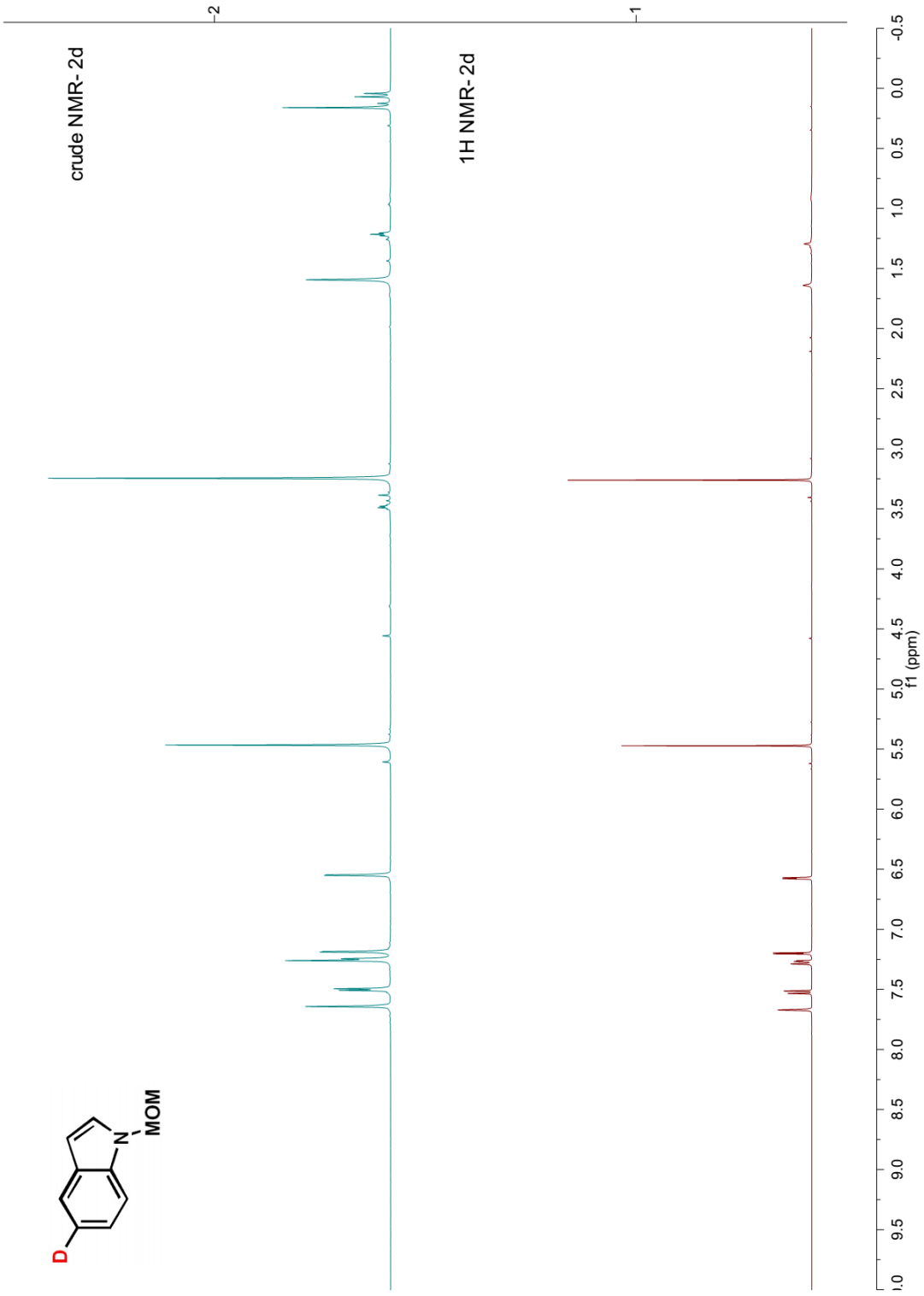
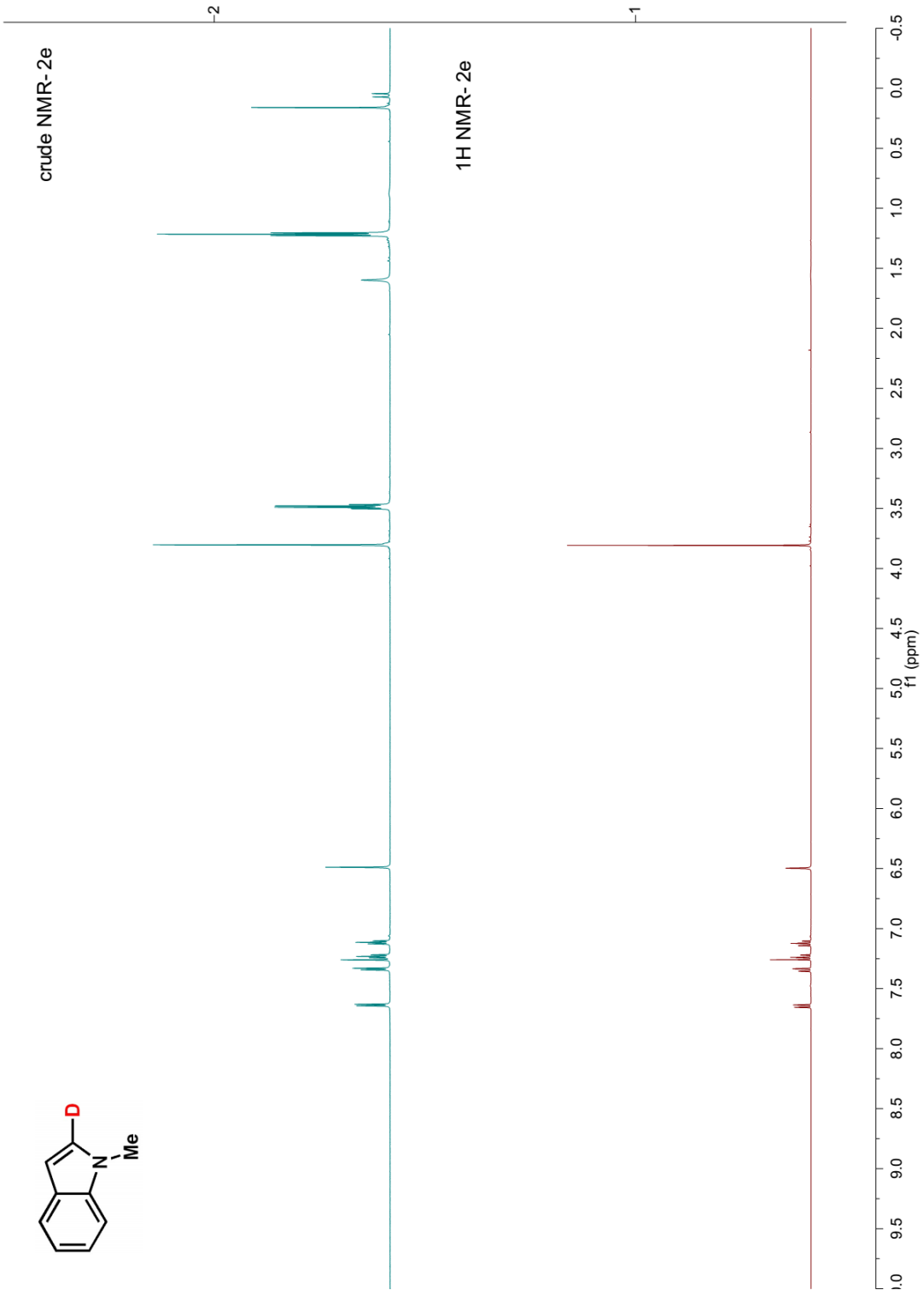
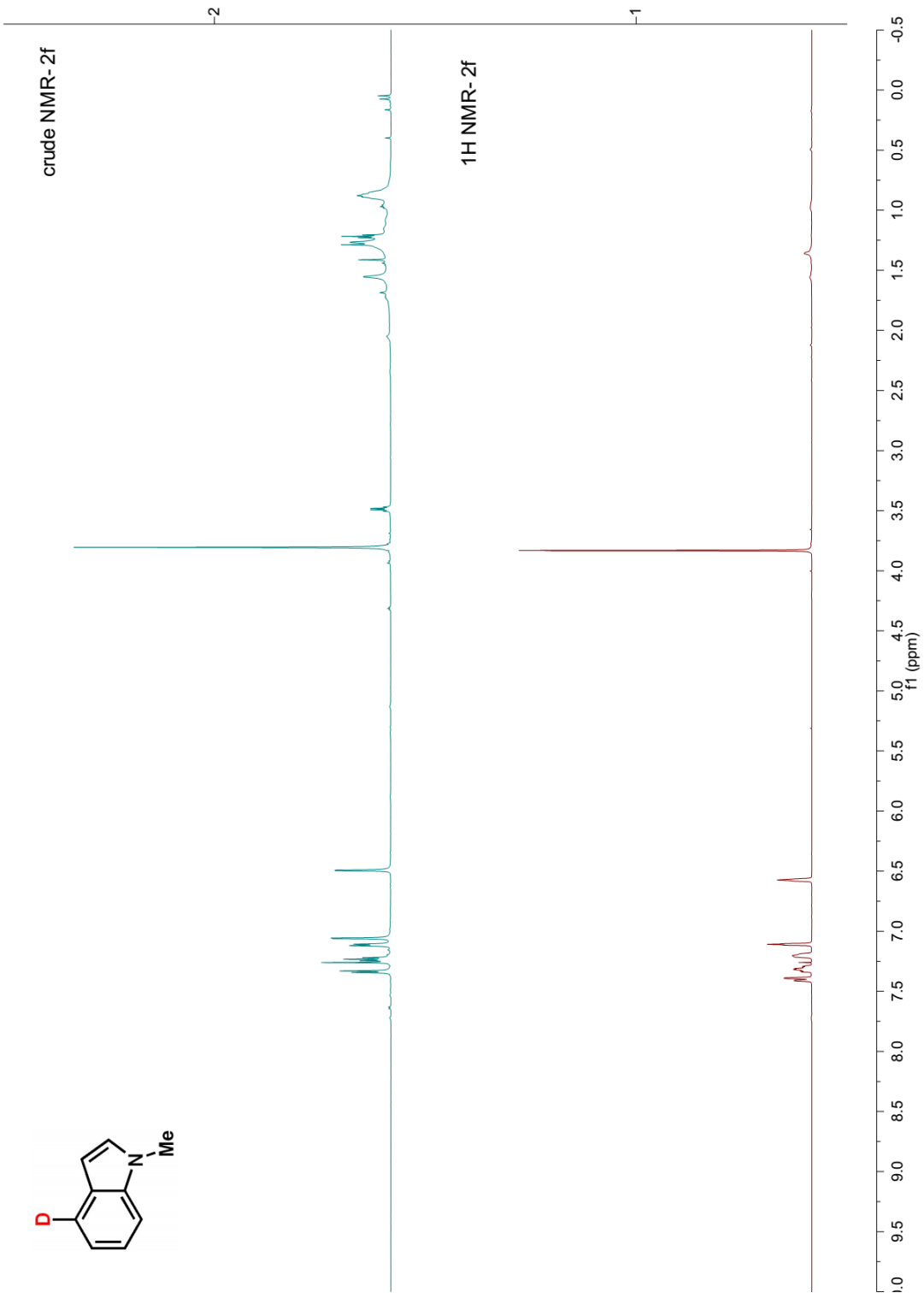
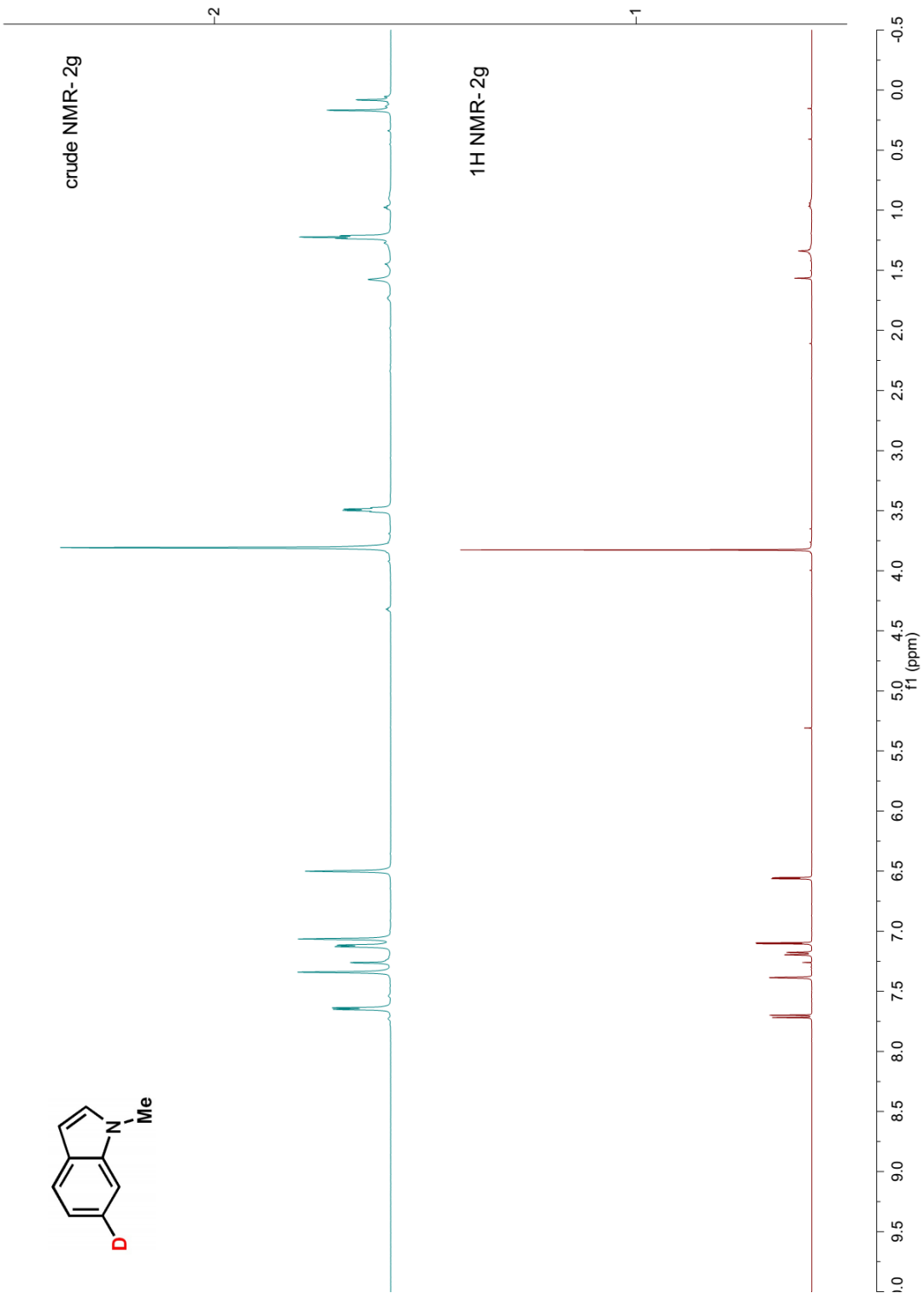
1H NMR- 2b
2
1
D
N
Bn
f1 (ppm)
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5

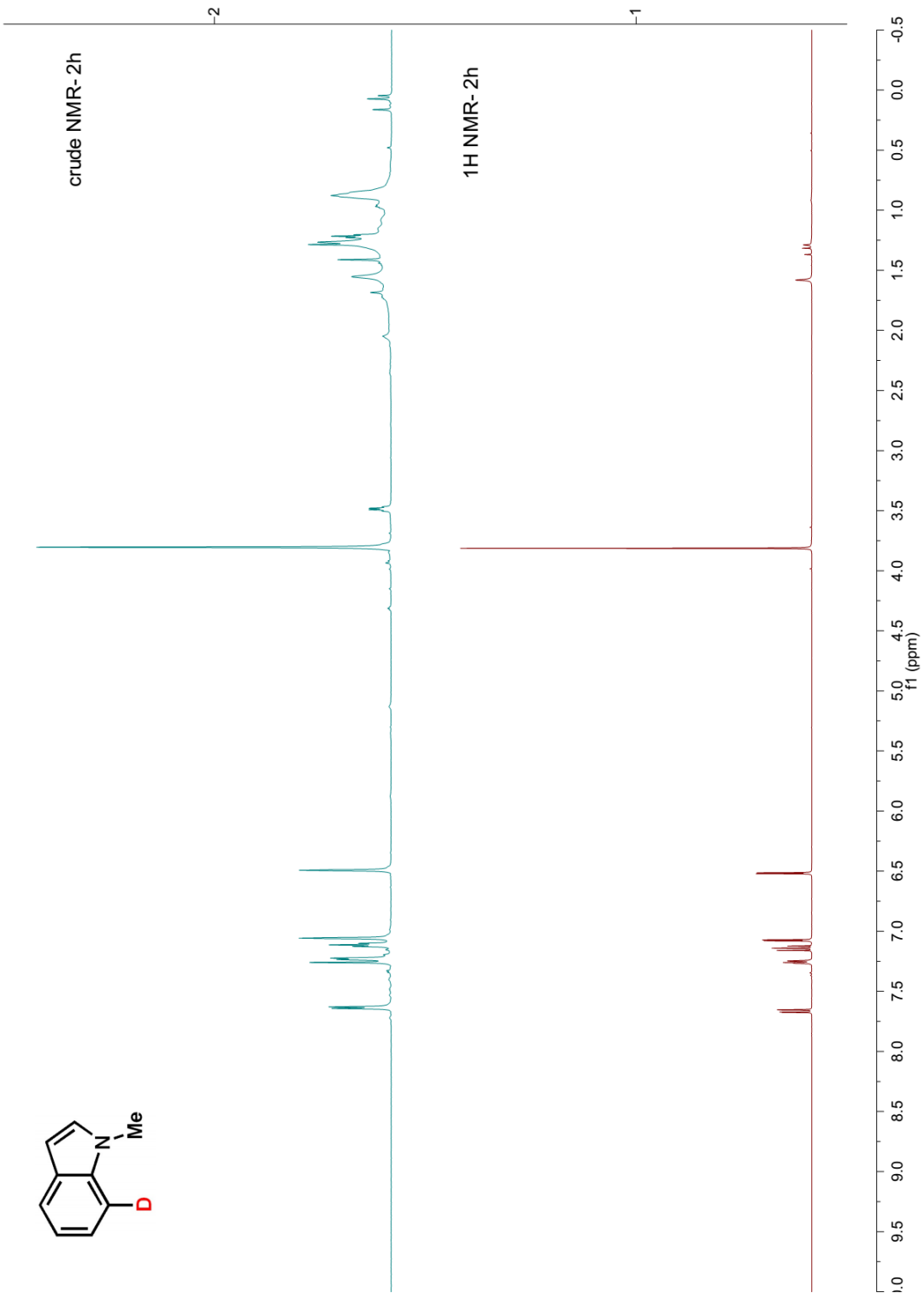

crude NMR- 2c
1H NMR- 2c
f1 (ppm)
D
N

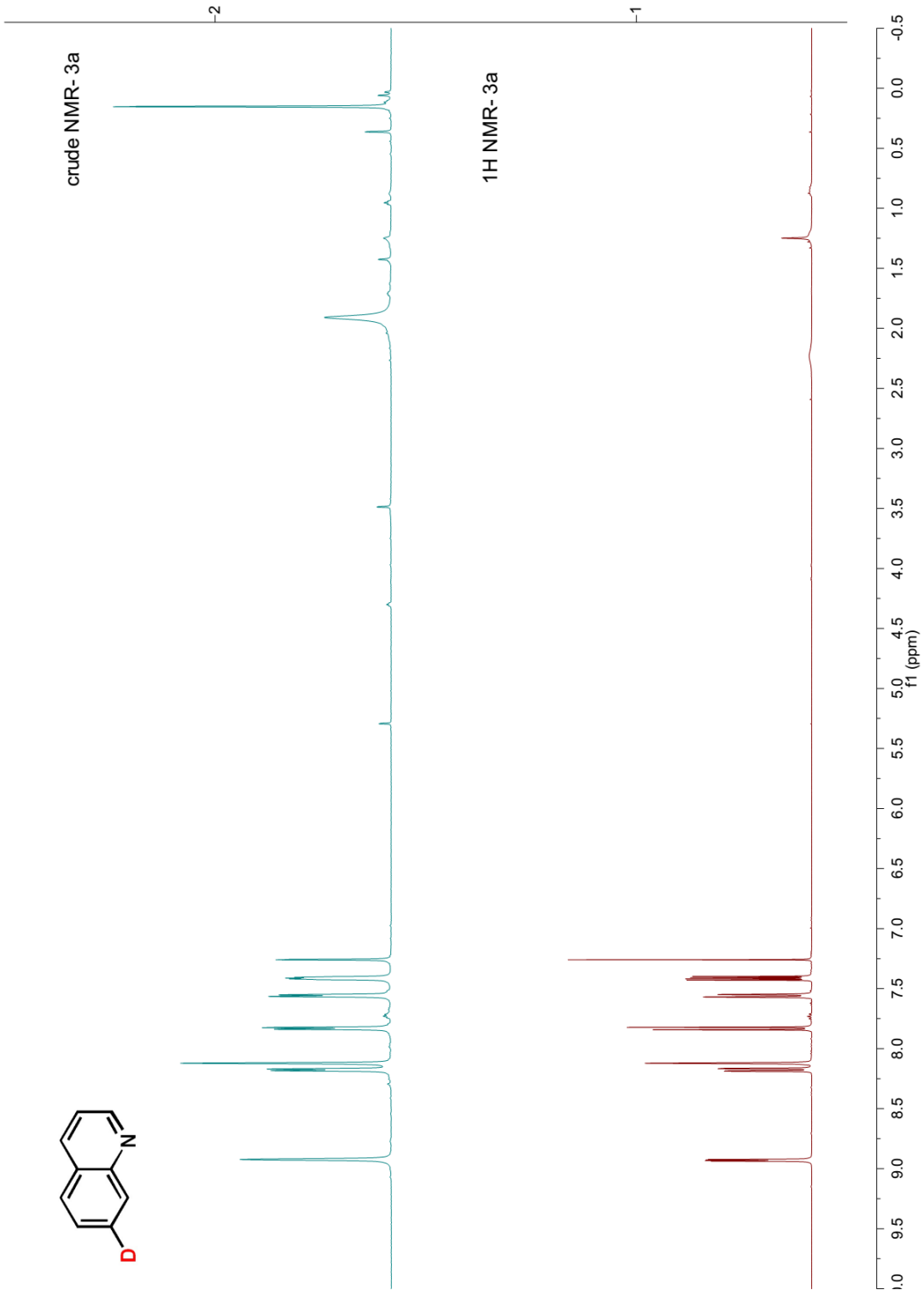

crude NMR- 2d
1H NMR- 2d
MOM
D
f1 (ppm)

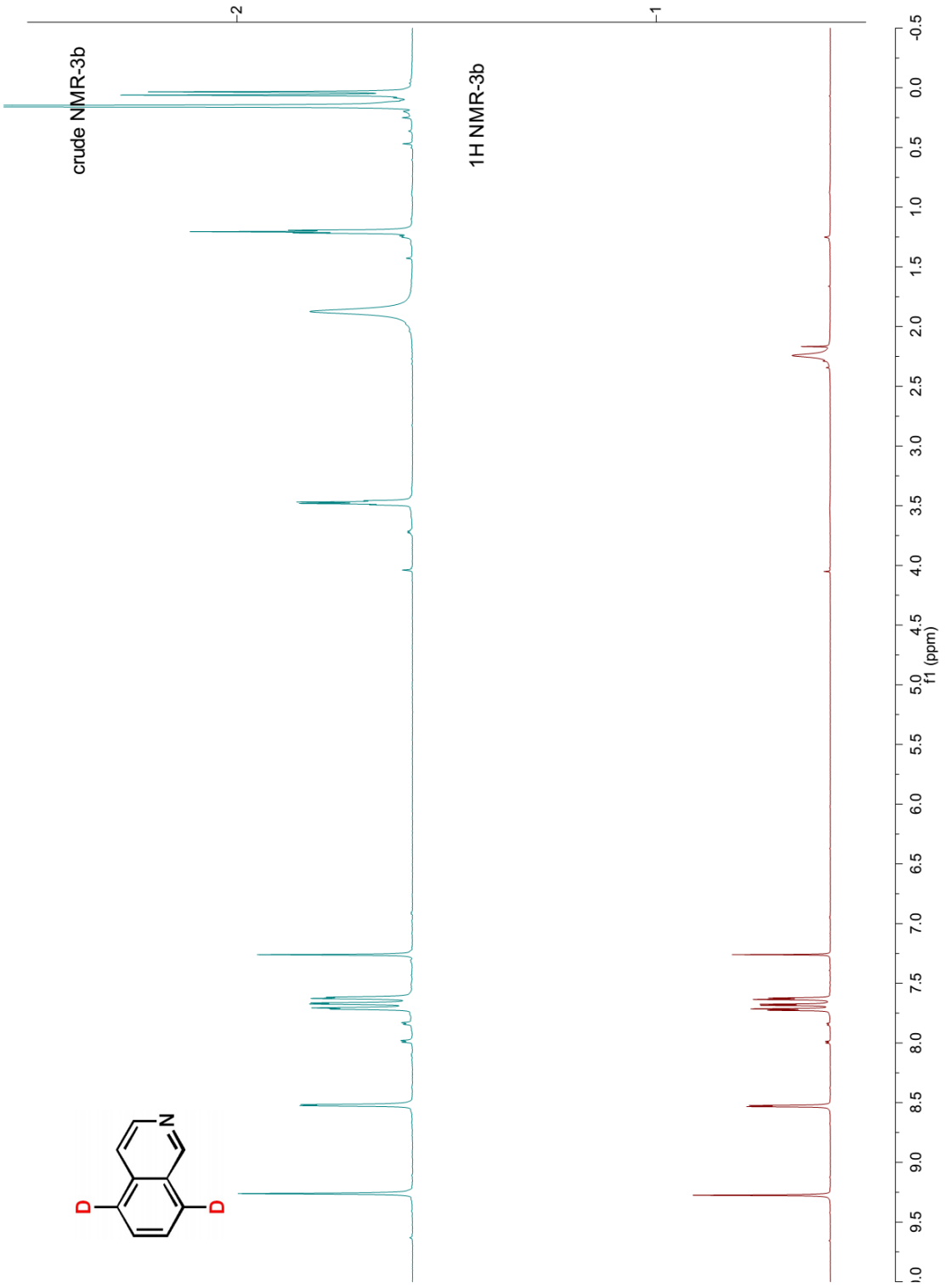

crude NMR- 2e
1H NMR- 2e
D
N
Me
f1 (ppm)

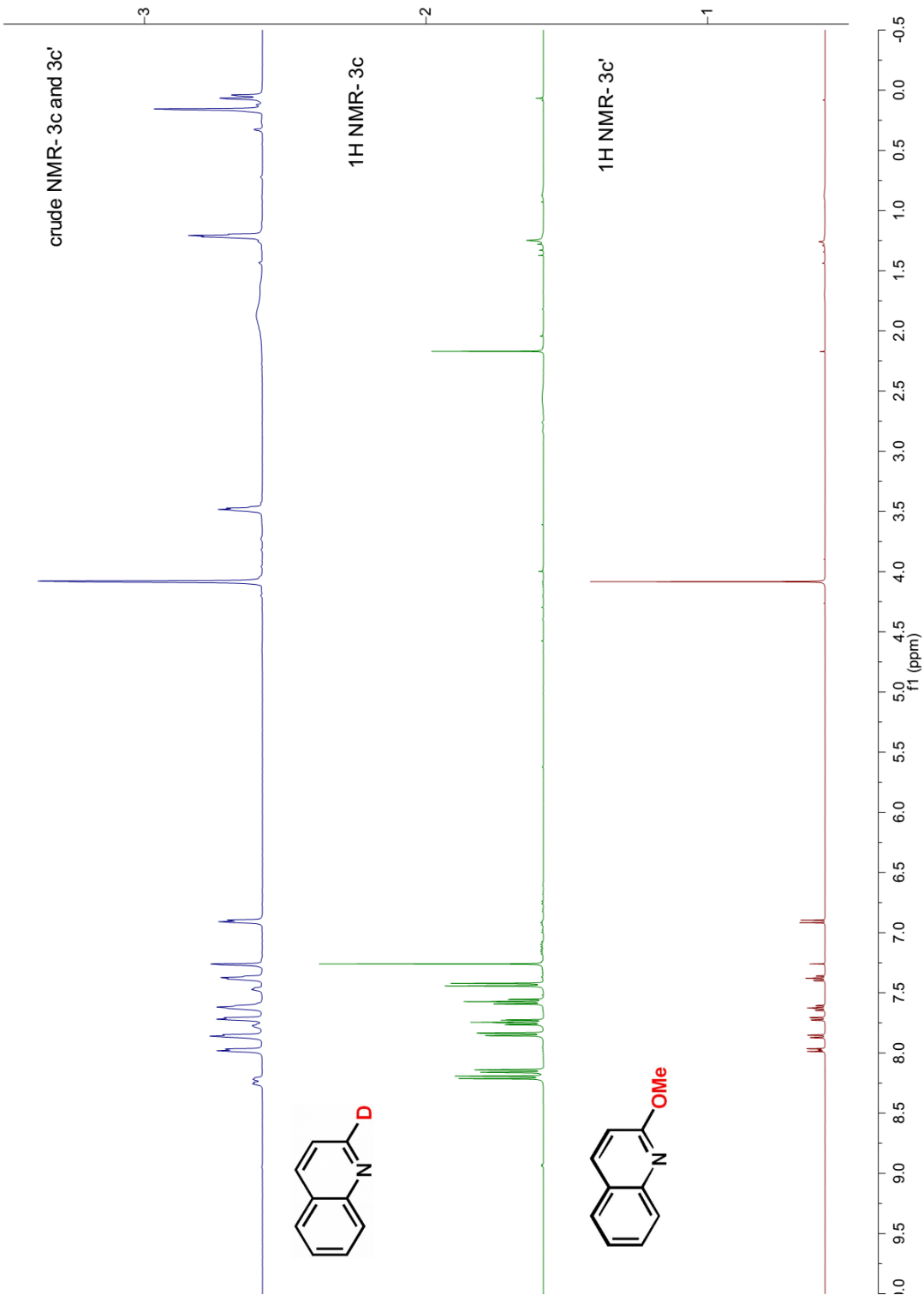

crude NMR- 2f
1H NMR- 2f
Me
D
f1 (ppm)

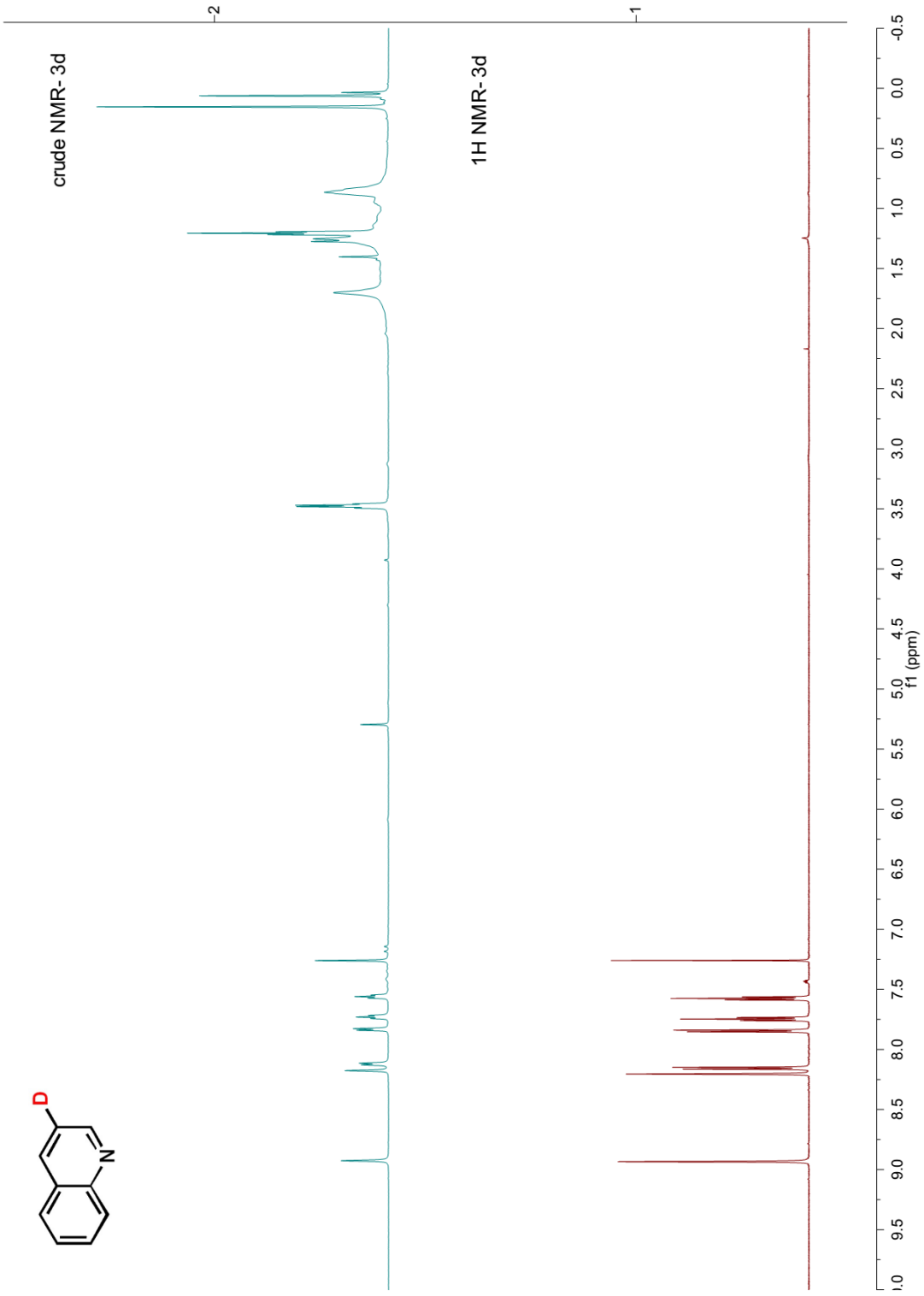

crude NMR- 2g
1H NMR- 2g
Me
N
D
f1 (ppm)

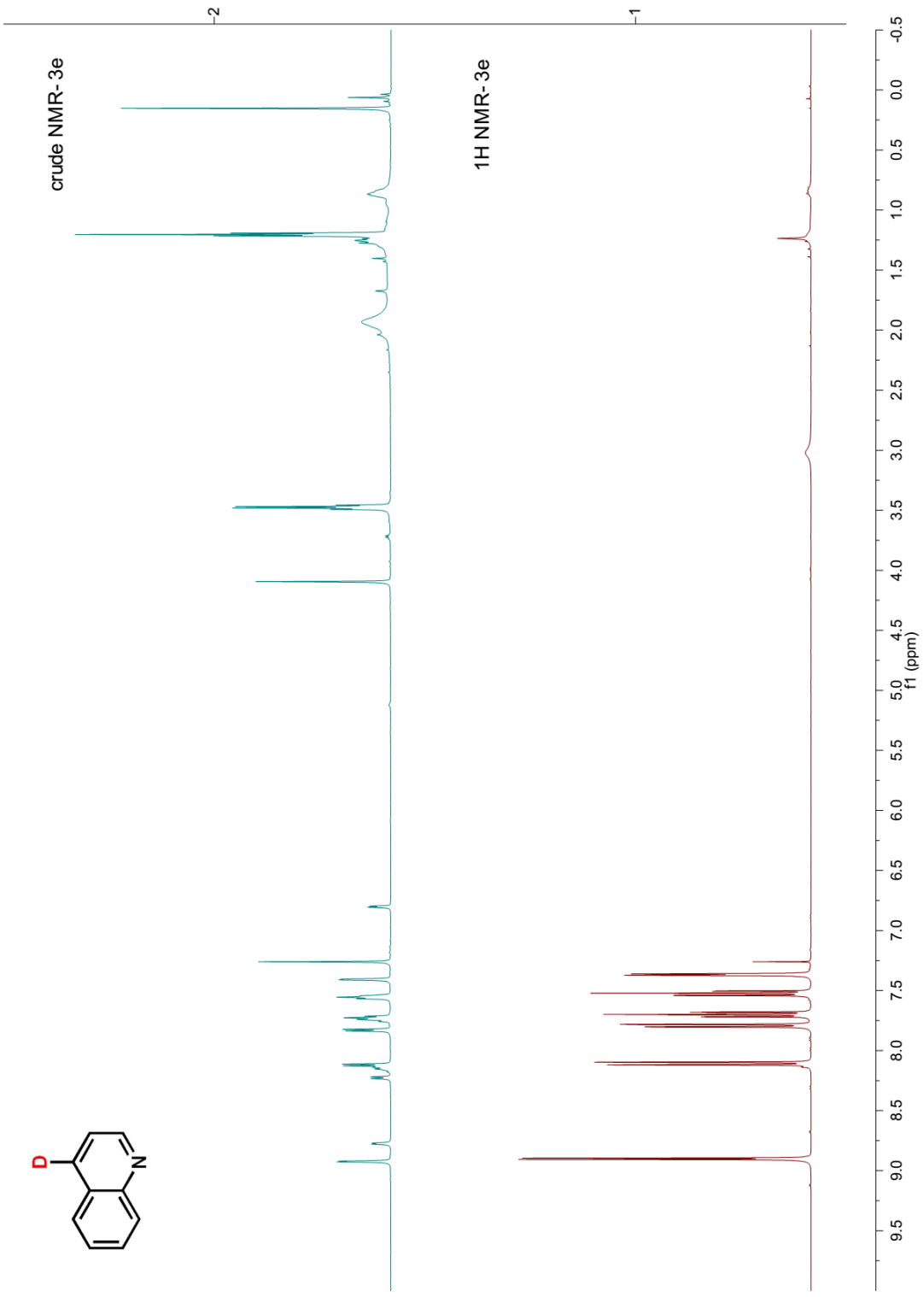

crude NMR- 2h
1H NMR- 2h
N
Me
D
f1 (ppm)

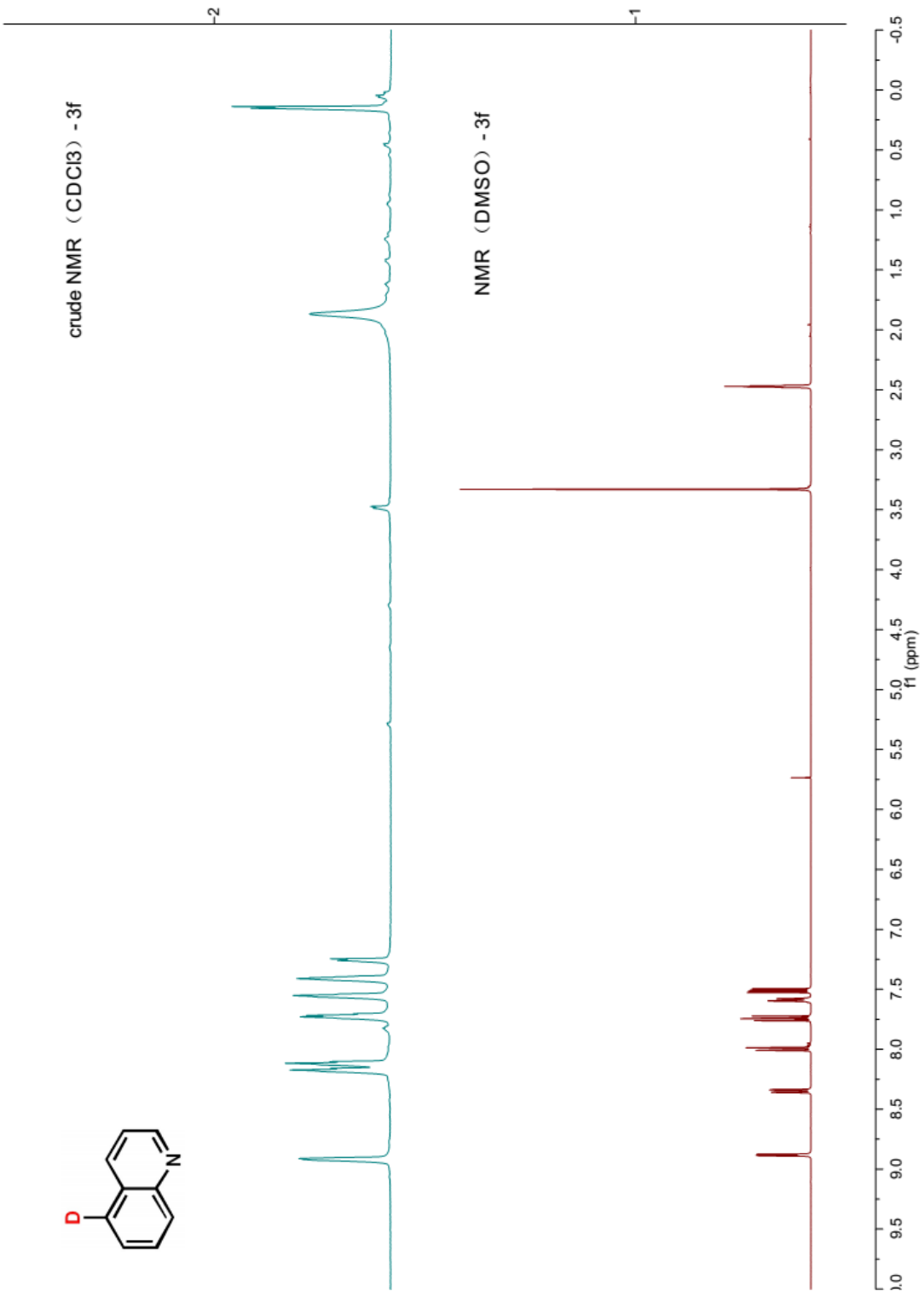

crude NMR- 3a
1H NMR- 3a
N
D
f1 (ppm)

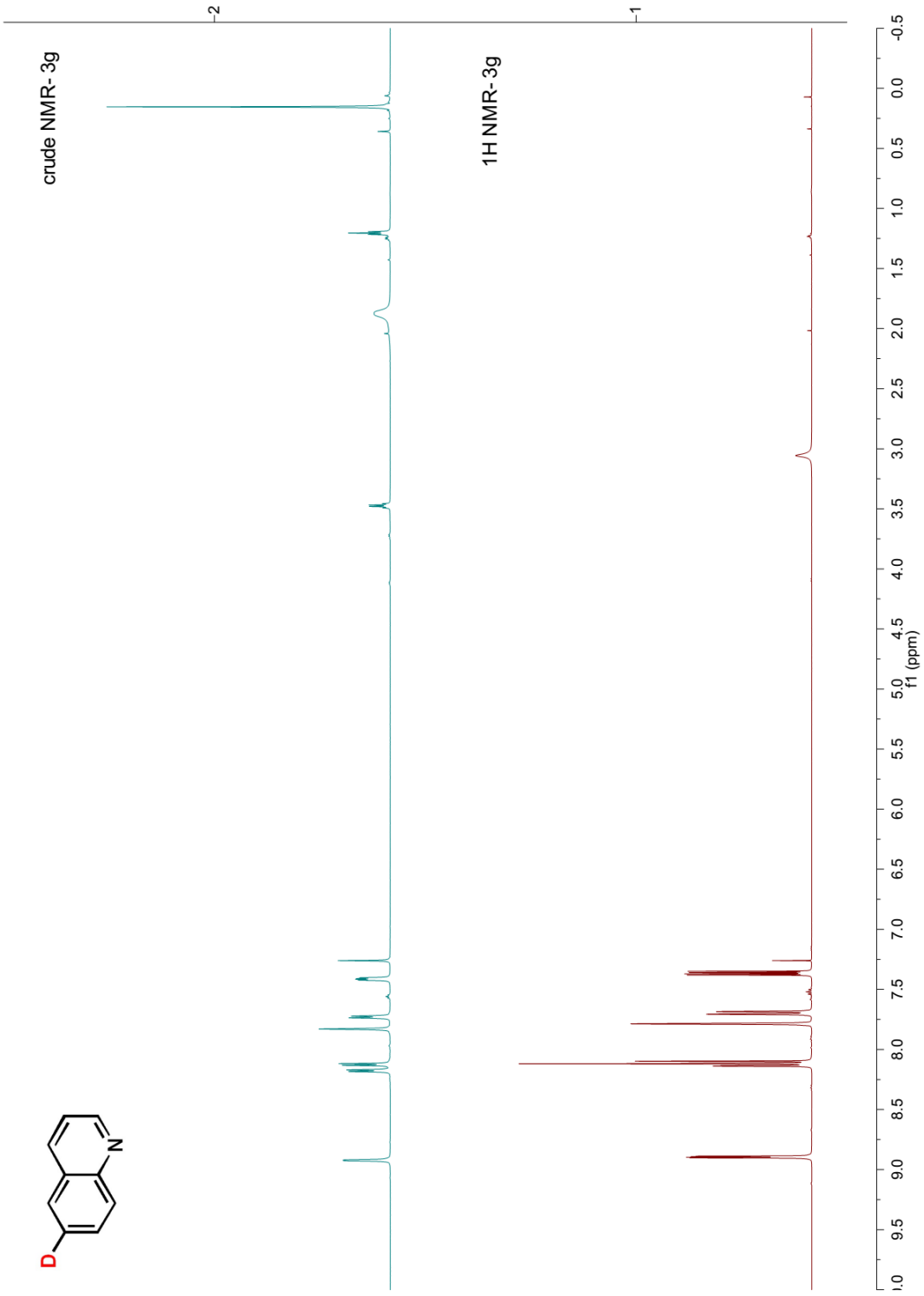

crude NMR-3b
1H NMR-3b
N
D
D
f1 (ppm)

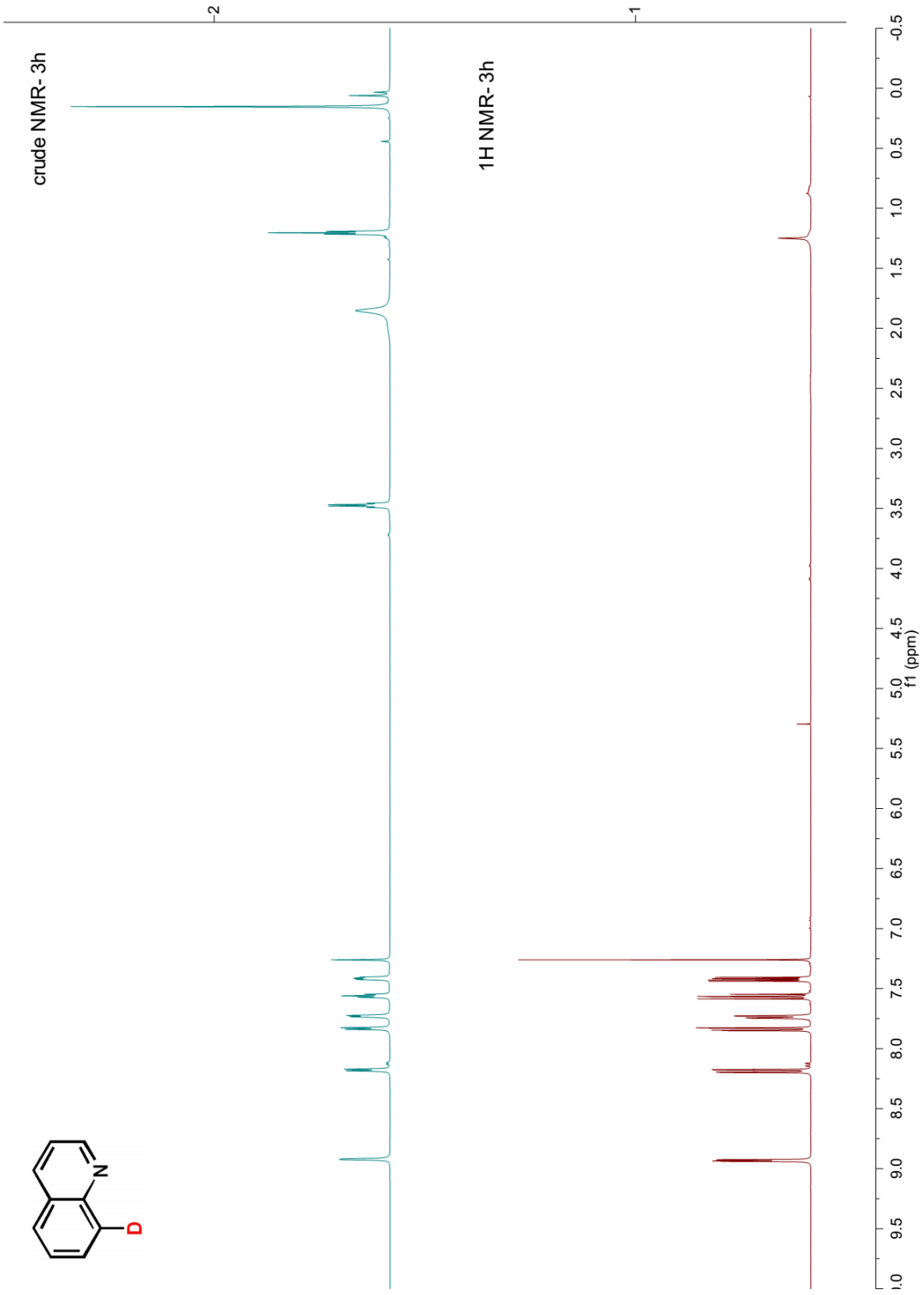

crude NMR- 3c and 3c'
1H NMR- 3c
1H NMR- 3c'
D
OMe
N
N
f1 (ppm)

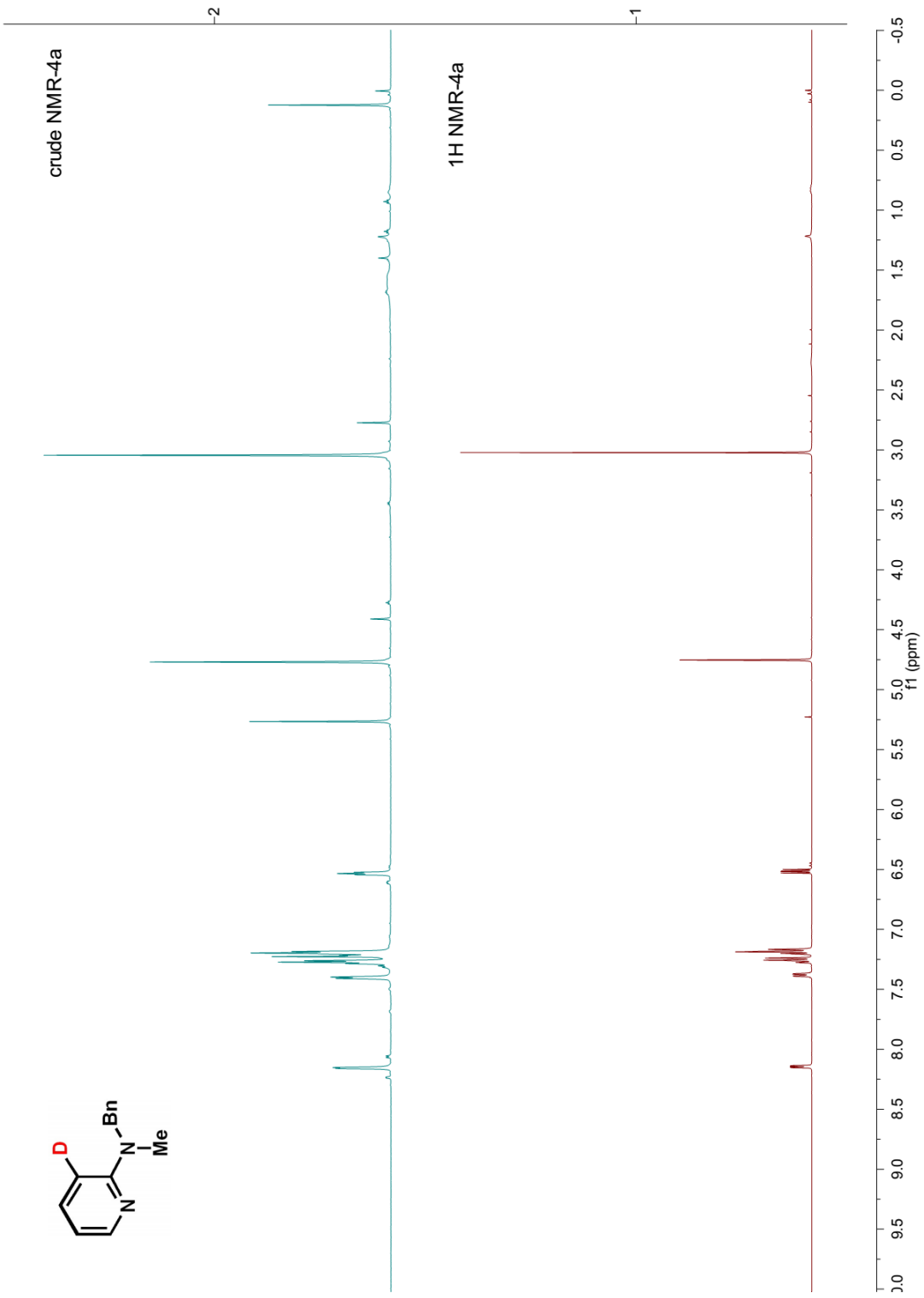

crude NMR- 3d
1H NMR- 3d
D
N
f1 (ppm)

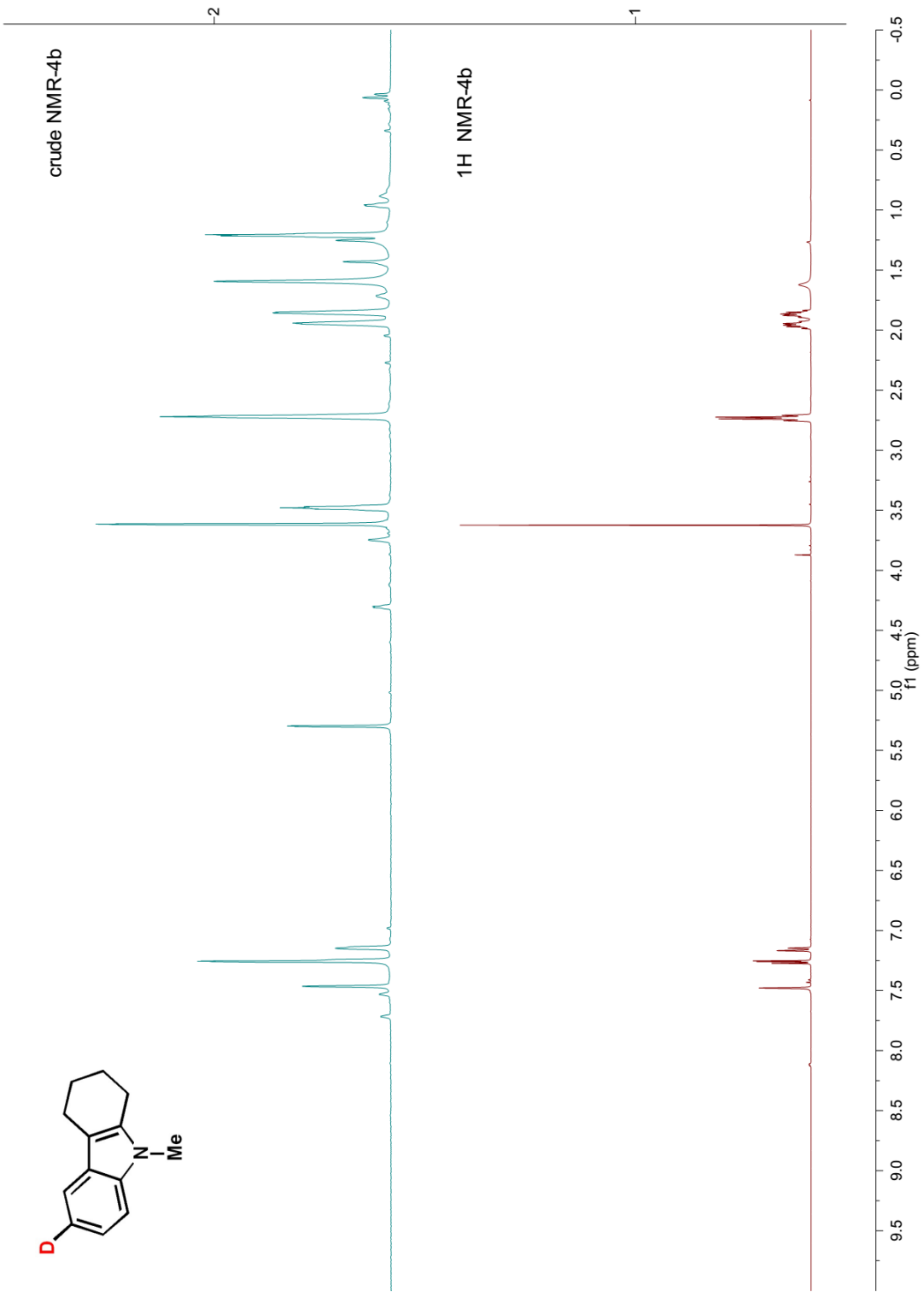

crude NMR-3e
1H NMR-3e
D
N
f1 (ppm)

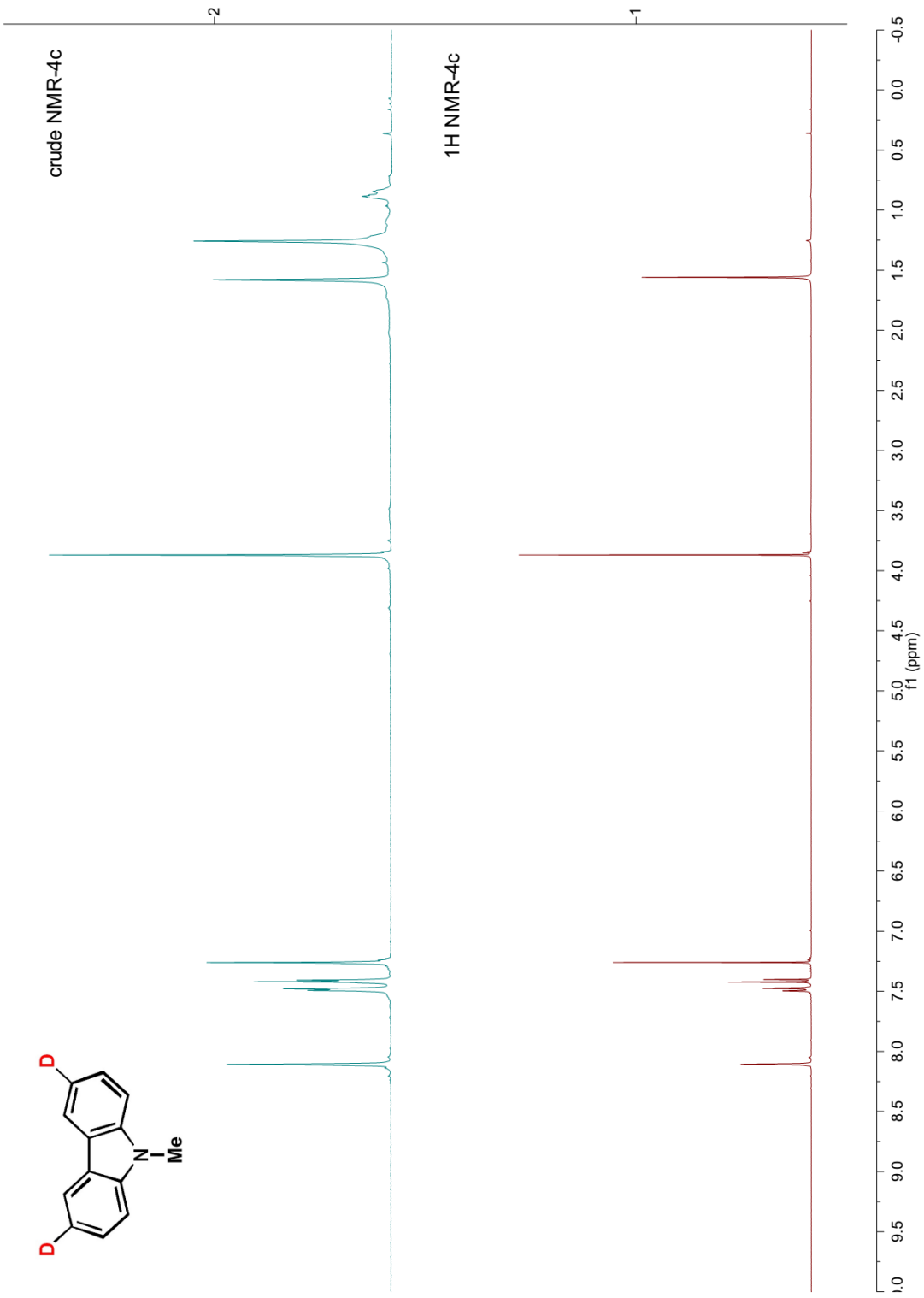

crude NMR（CDCl3）- 3f
NMR（DMSO）- 3f
D
N
f1 (ppm)

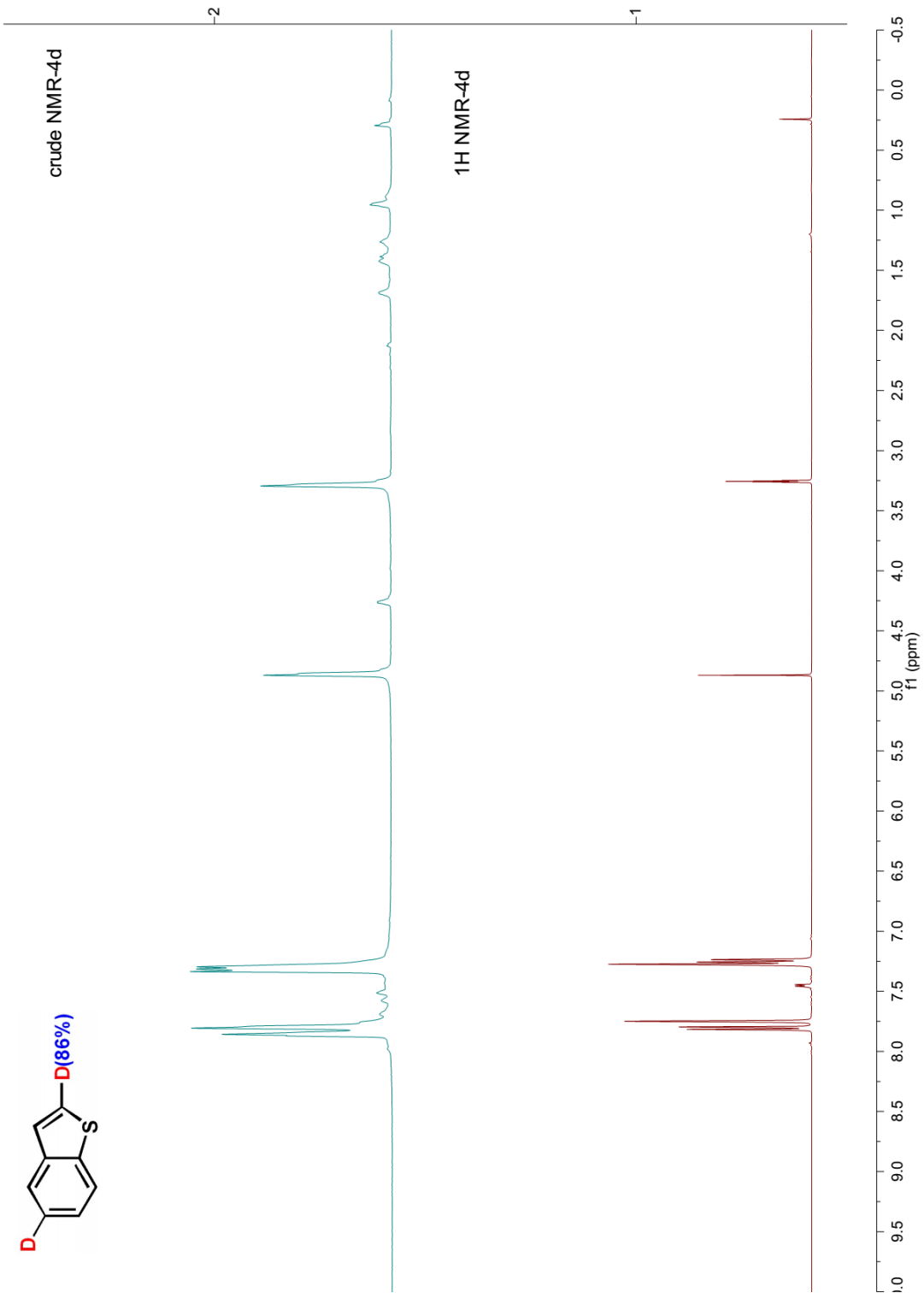

crude NMR- 3g
1H NMR- 3g
f1 (ppm)
D
N

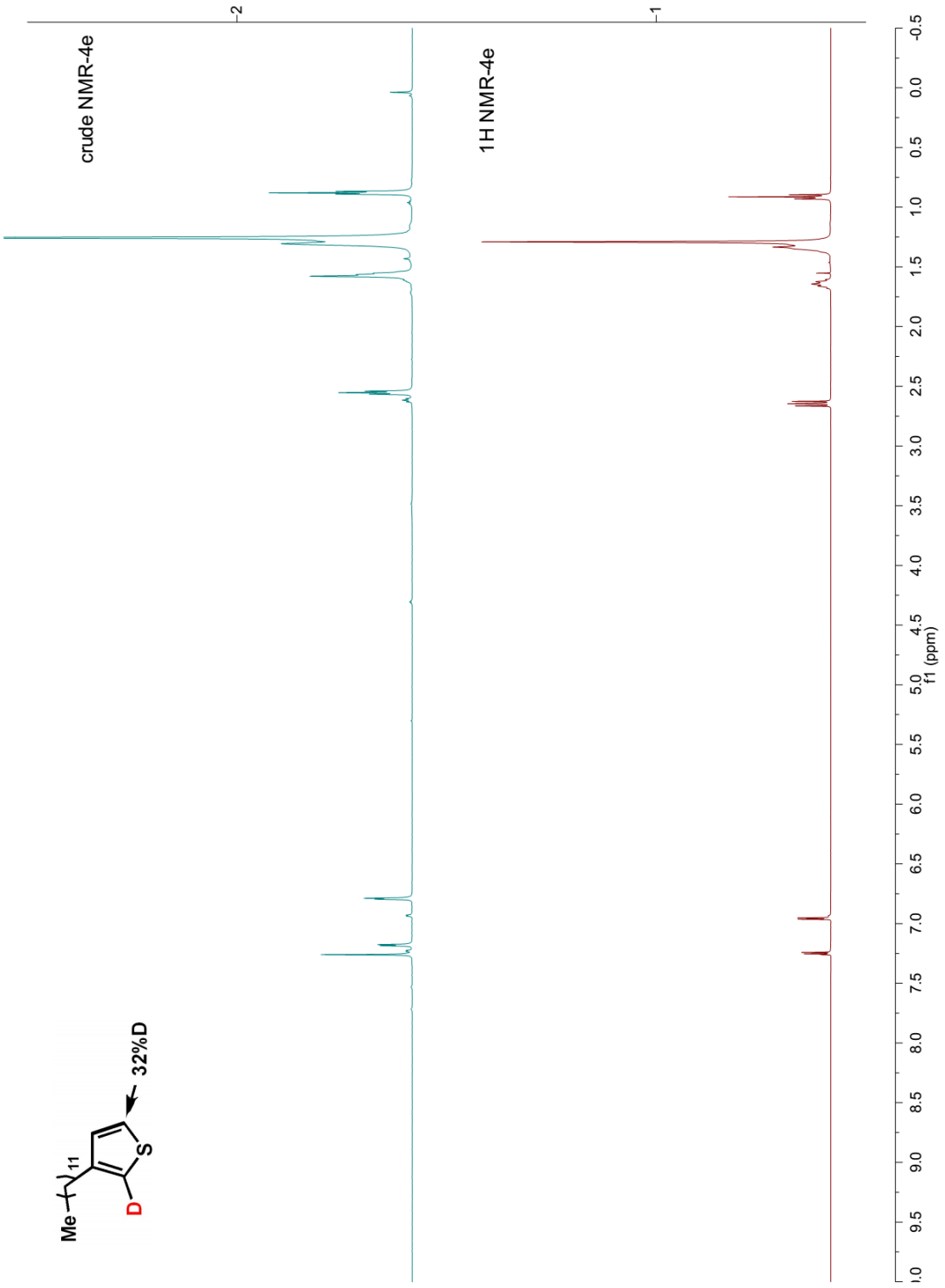

crude NMR- 3h
1H NMR- 3h
2
1
D
N
f1 (ppm)
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0

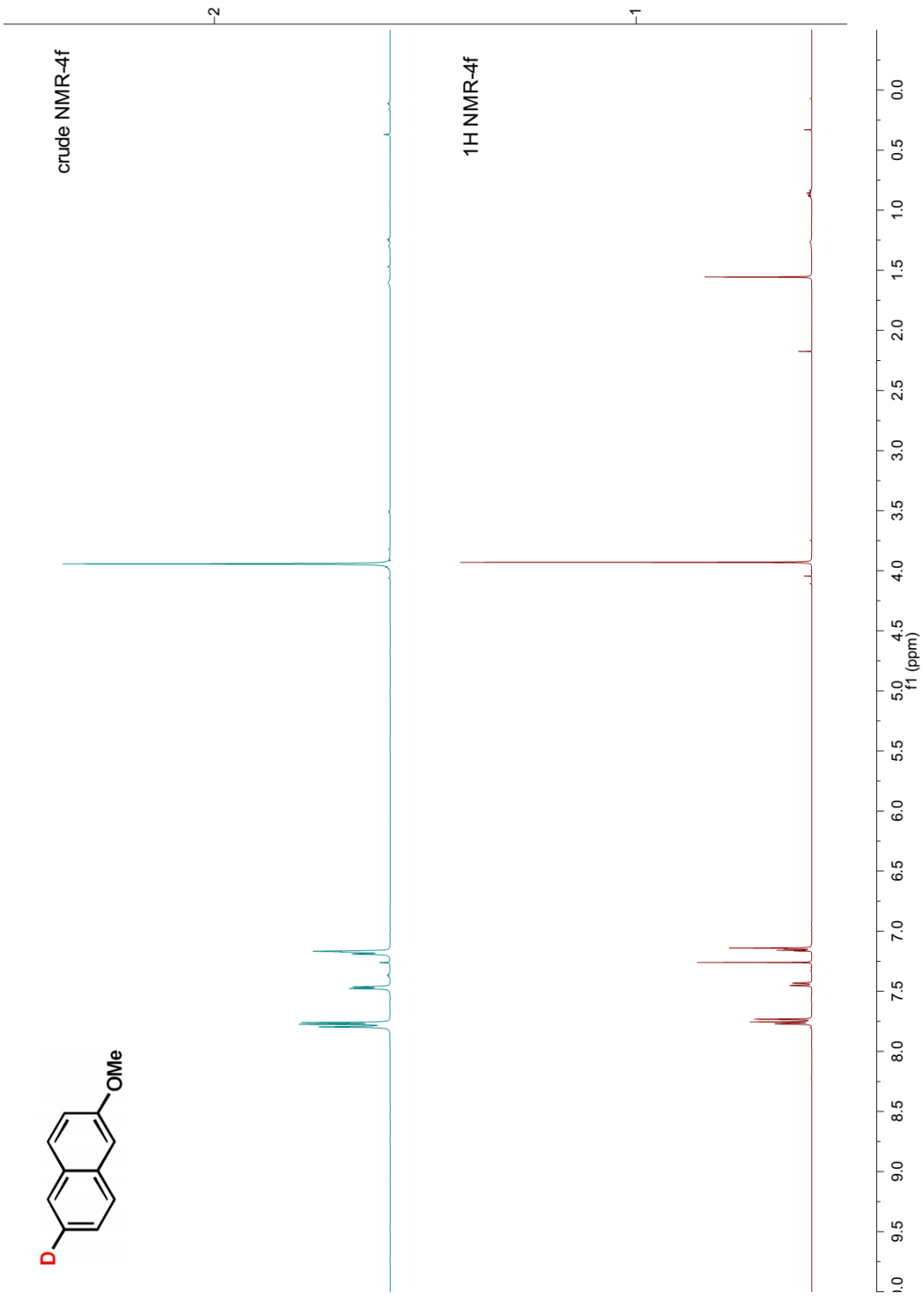

crude NMR-4a
1H NMR-4a
D
N
Bn
Me
f1 (ppm)

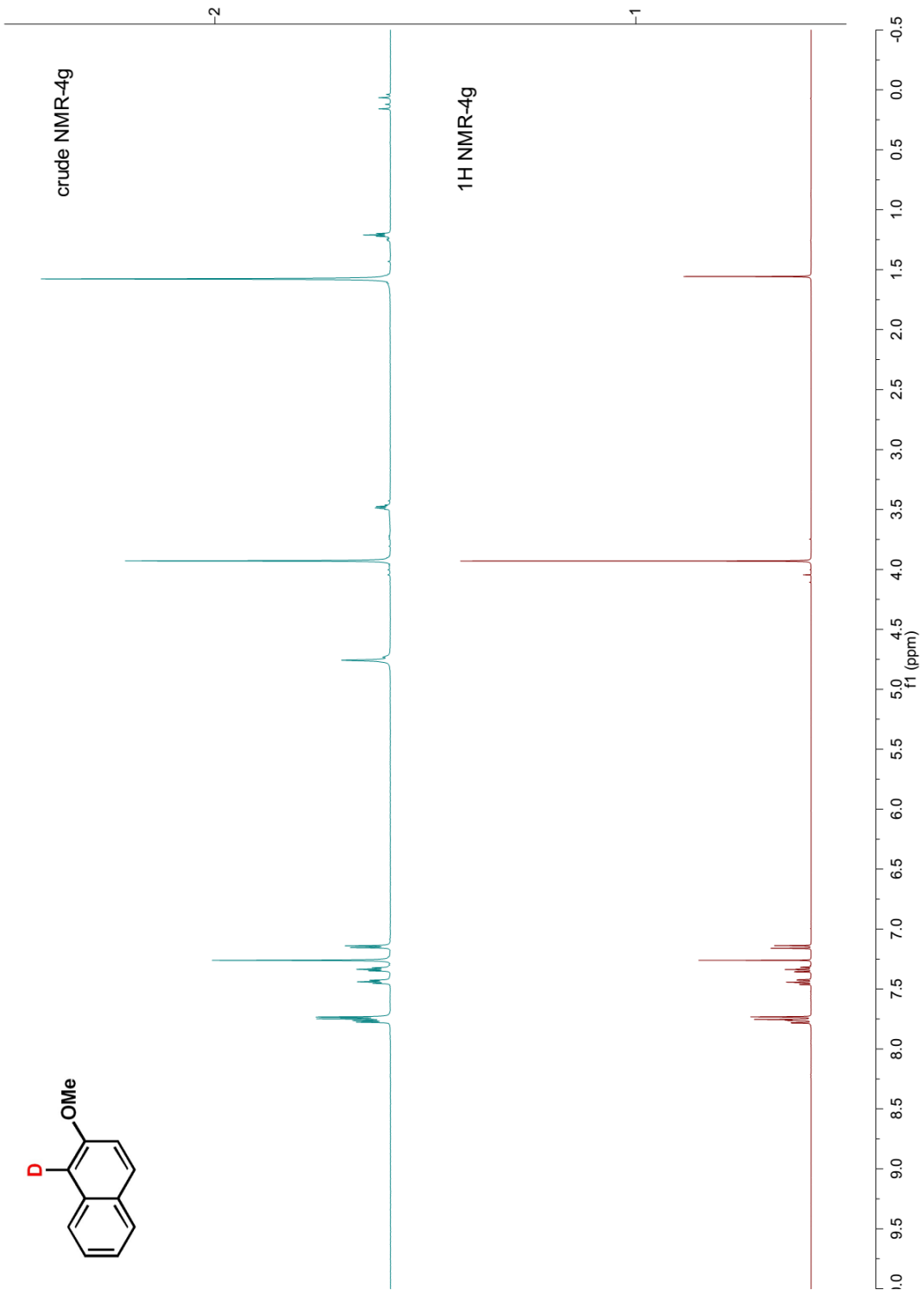

crude NMR-4b
1H NMR-4b
2
1
N
Me
D
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

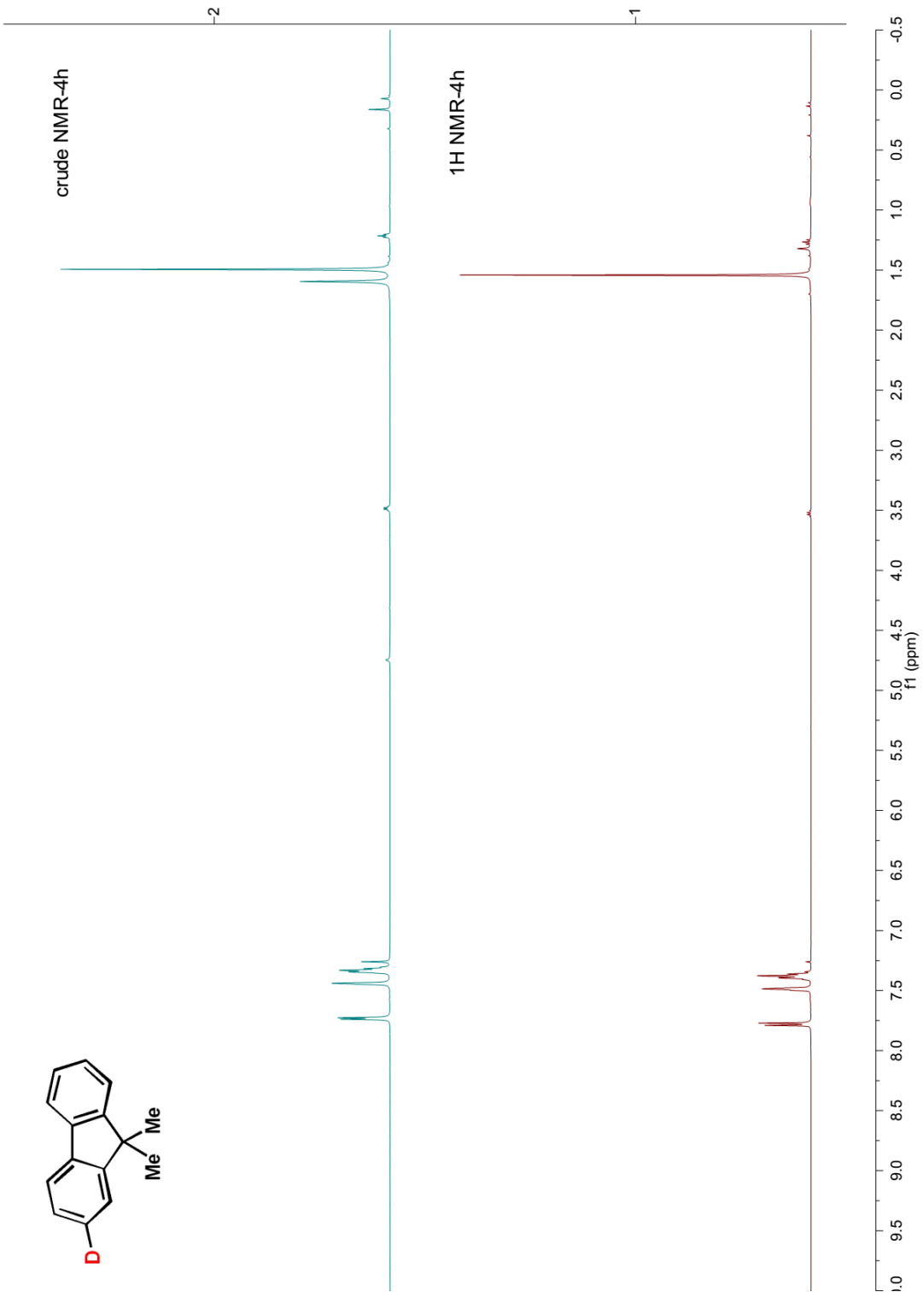

crude NMR-4c
1H NMR-4c
D
N
Me
D
f1 (ppm)

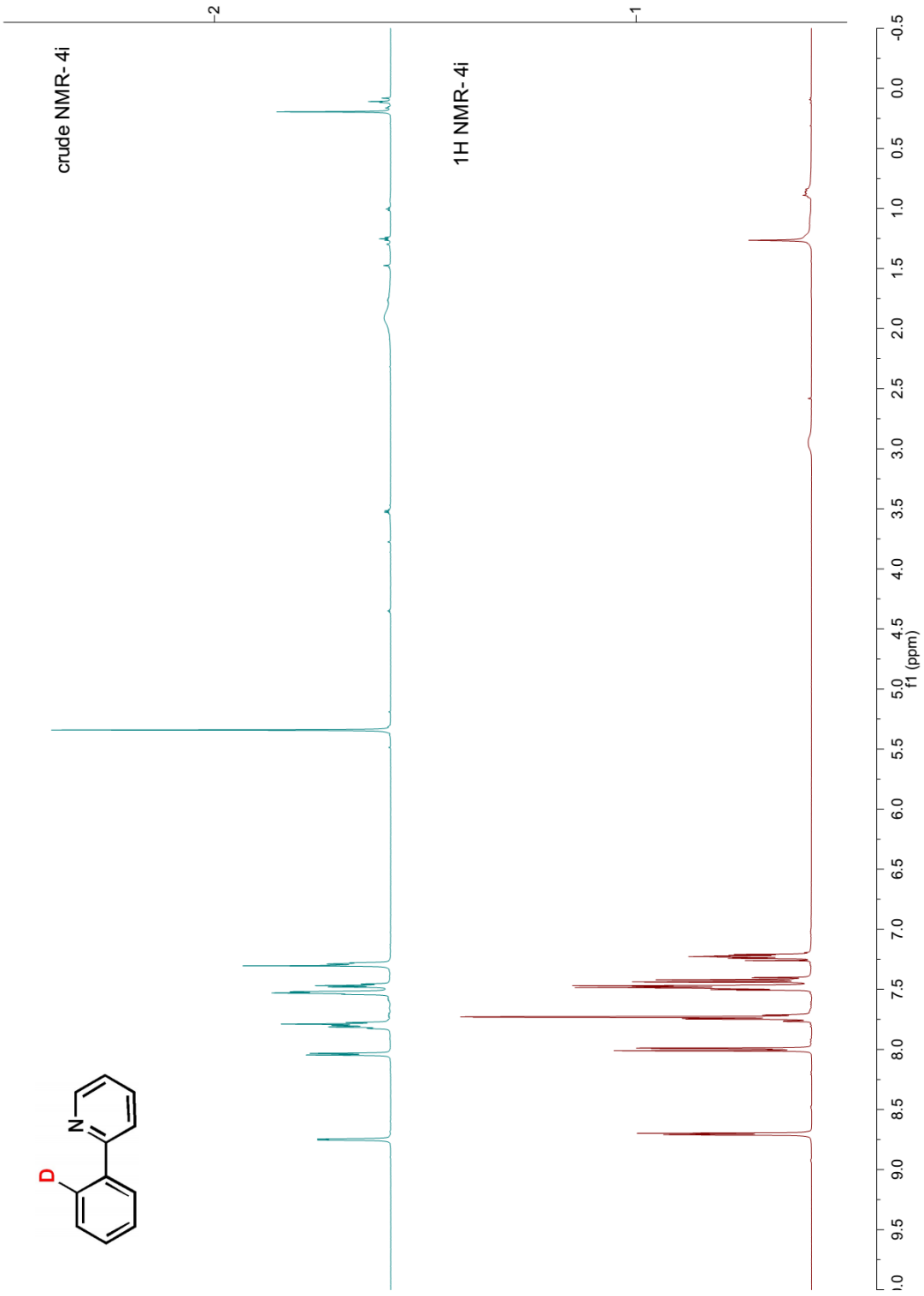

crude NMR-4d
1H NMR-4d
D(86%)
D
S
f1 (ppm)

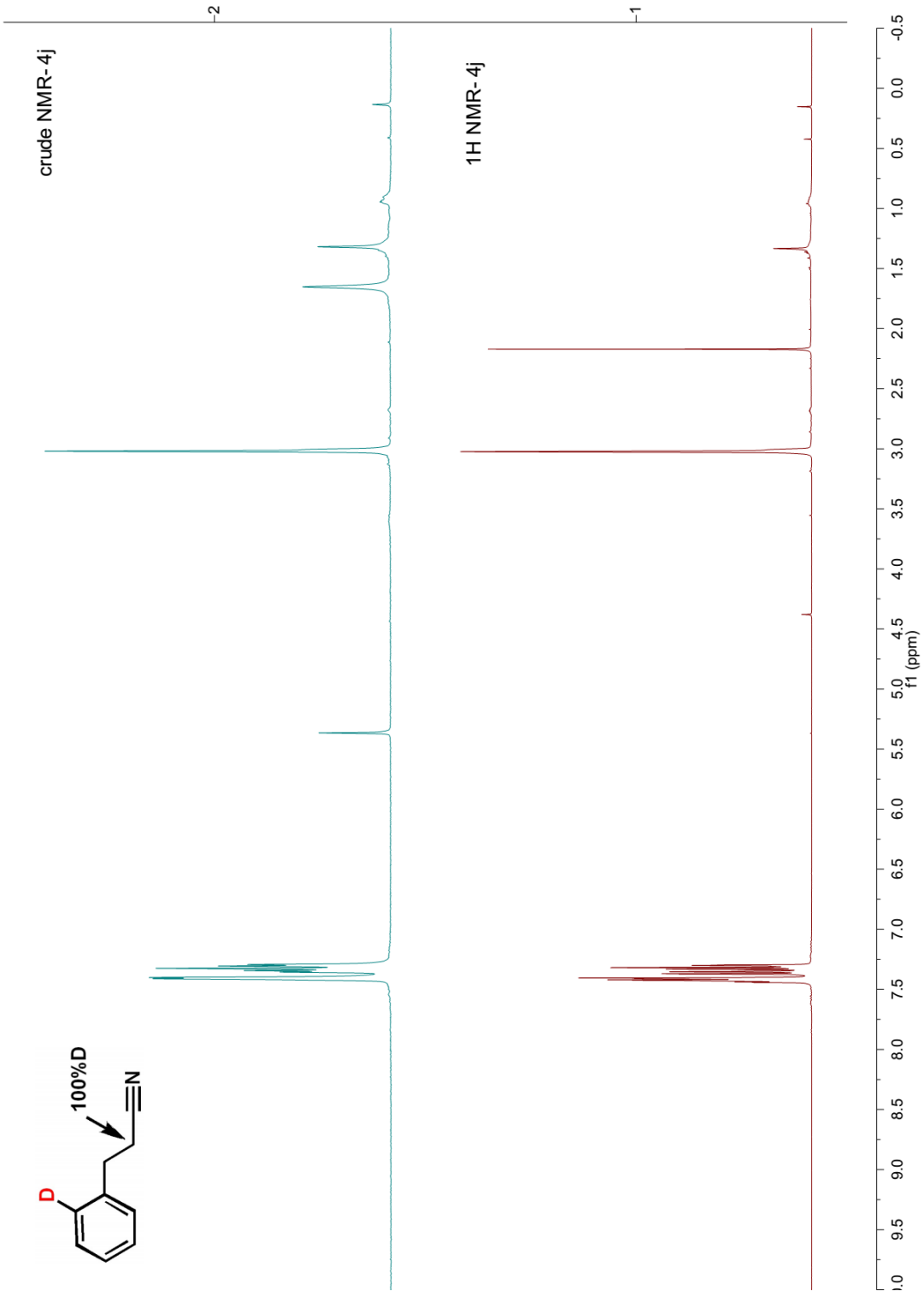

crude NMR-4e
1H NMR-4e
32%D
Me
11
D
S
f1 (ppm)

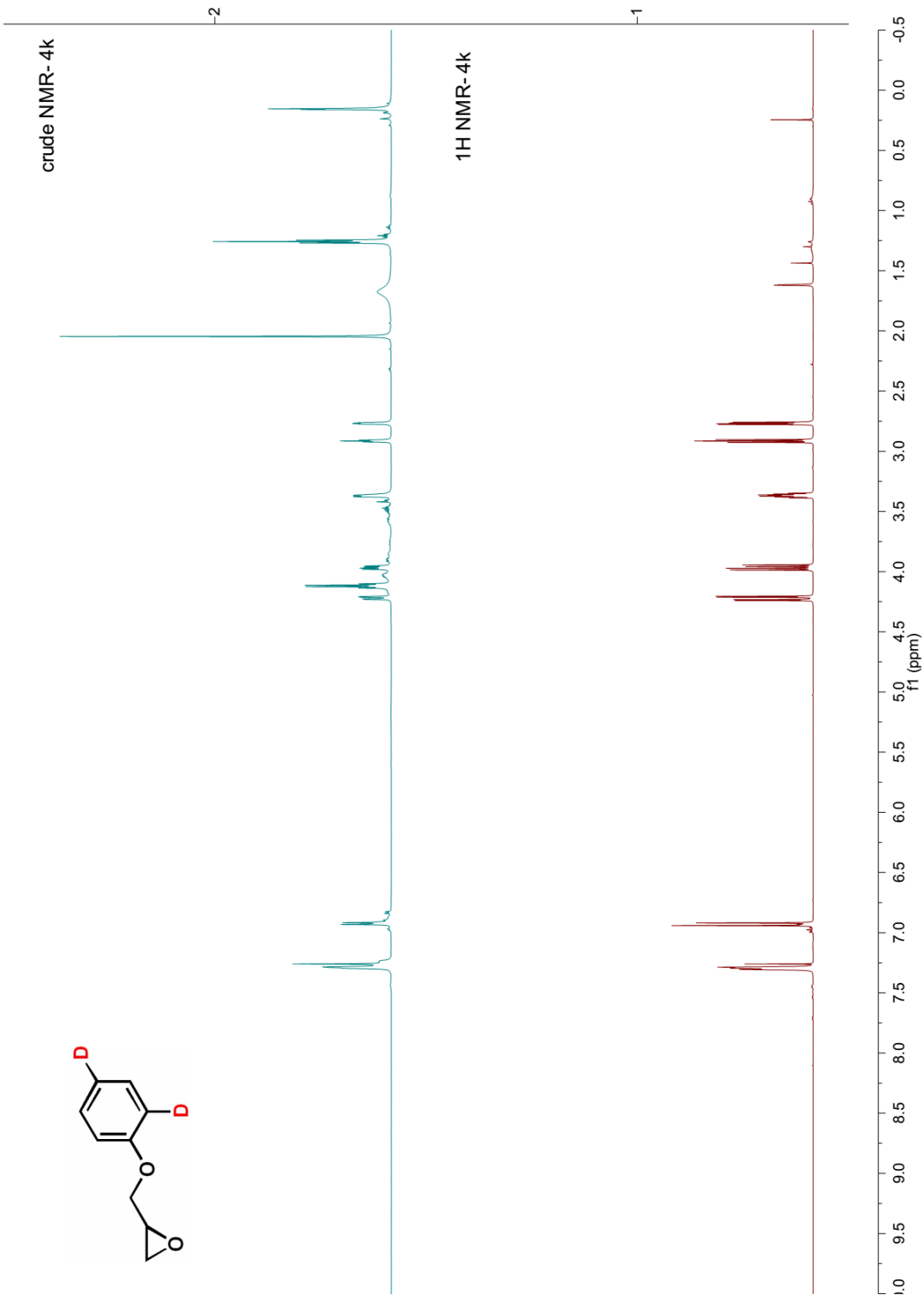

crude NMR-4f
1H NMR-4f
OMe
D
f1 (ppm)

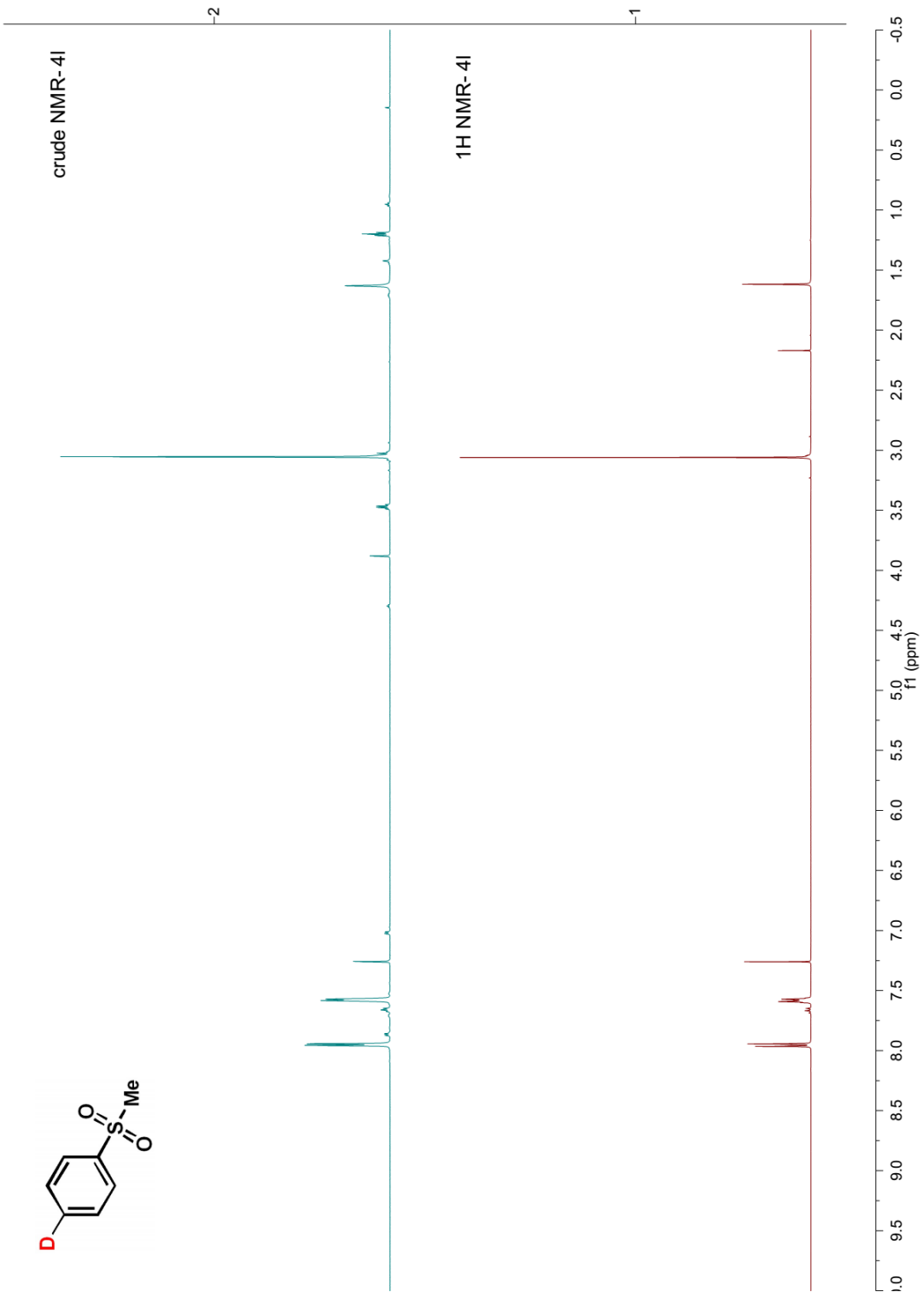

crude NMR-4g
1H NMR-4g
OMe
D
f1 (ppm)

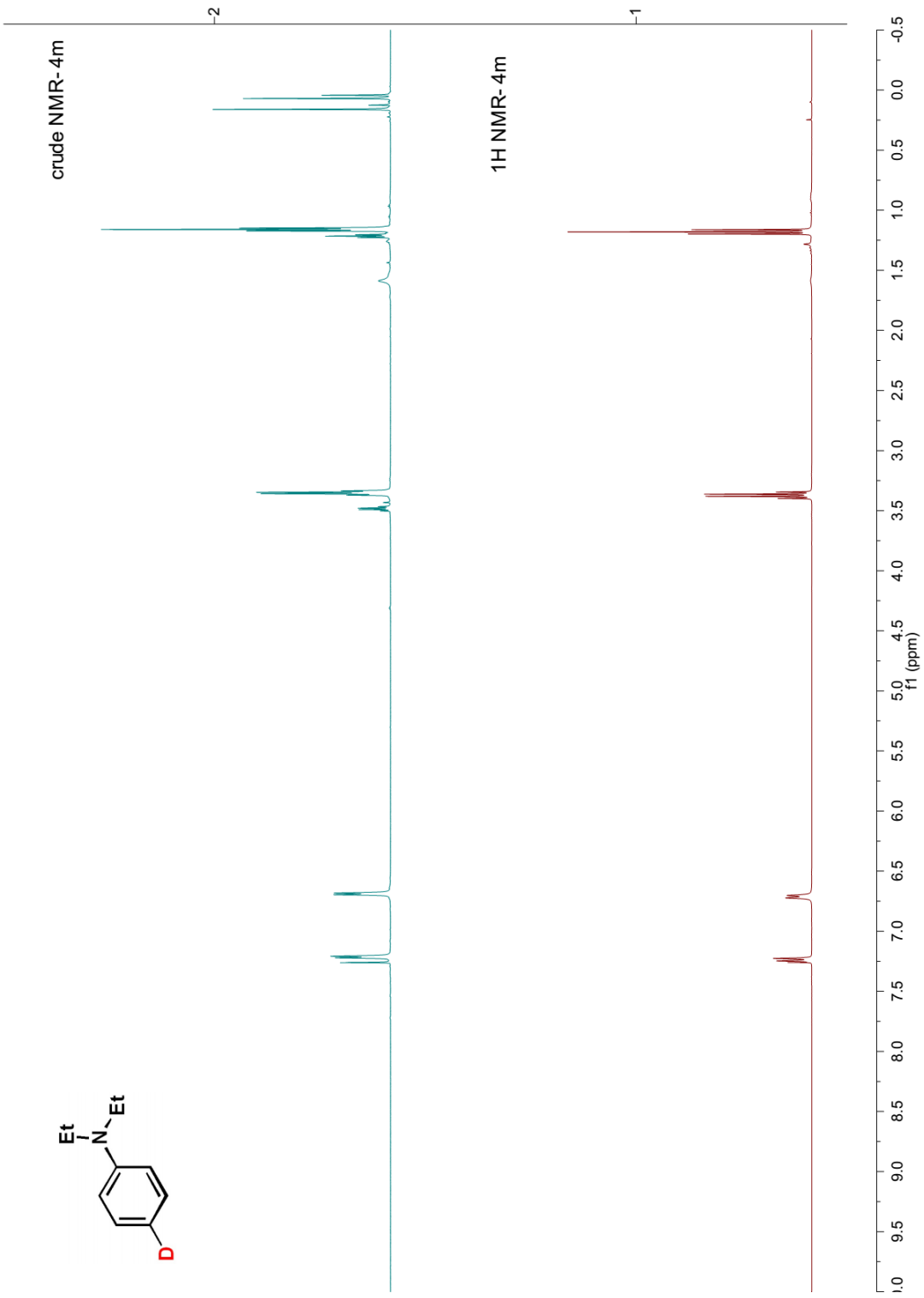

crude NMR-4h
1H NMR-4h
Me
Me
D
f1 (ppm)

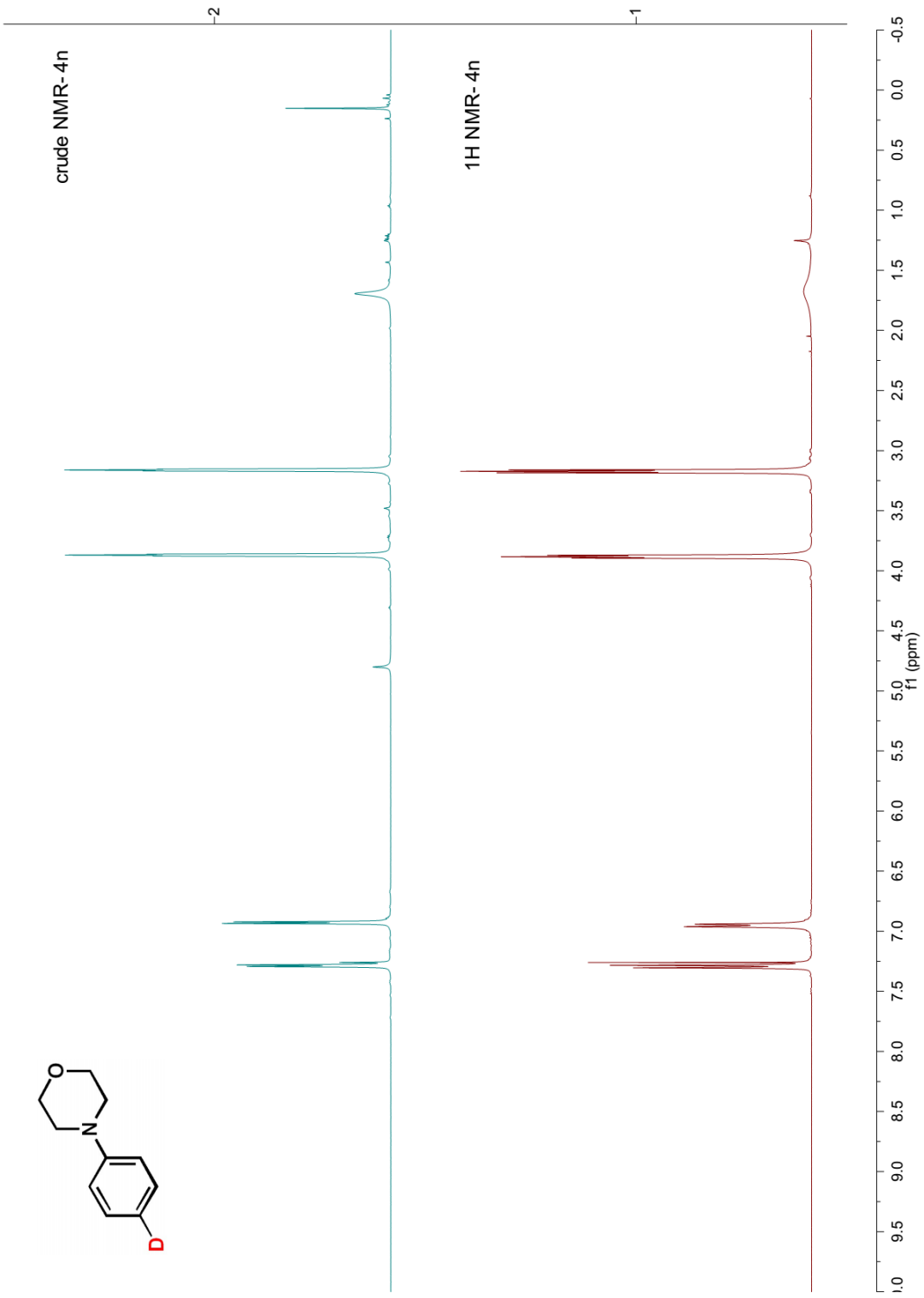

crude NMR-4i
1H NMR-4i
D
N
f1 (ppm)

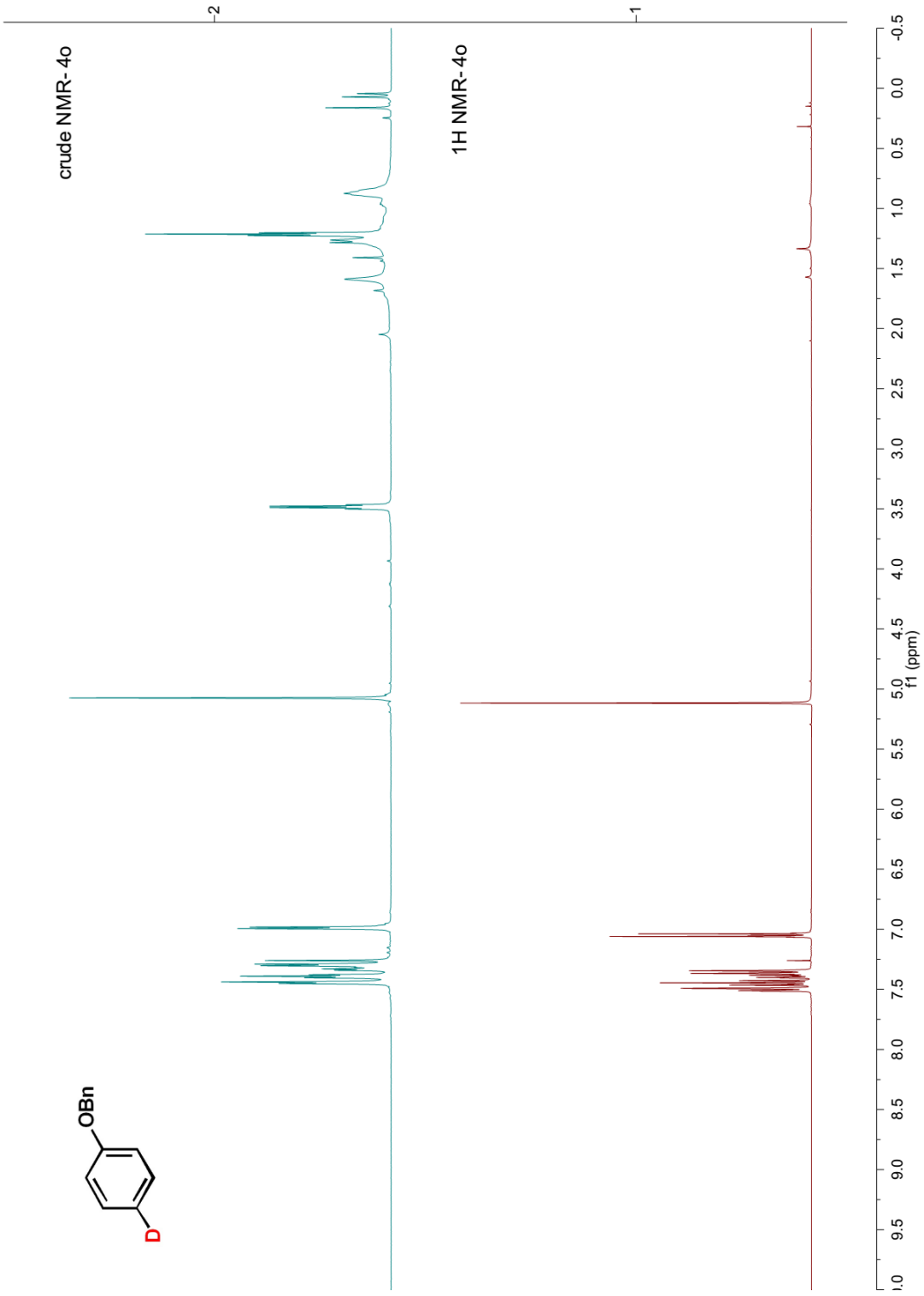

crude NMR-4j
1H NMR-4j
100%D
D
N
f1 (ppm)

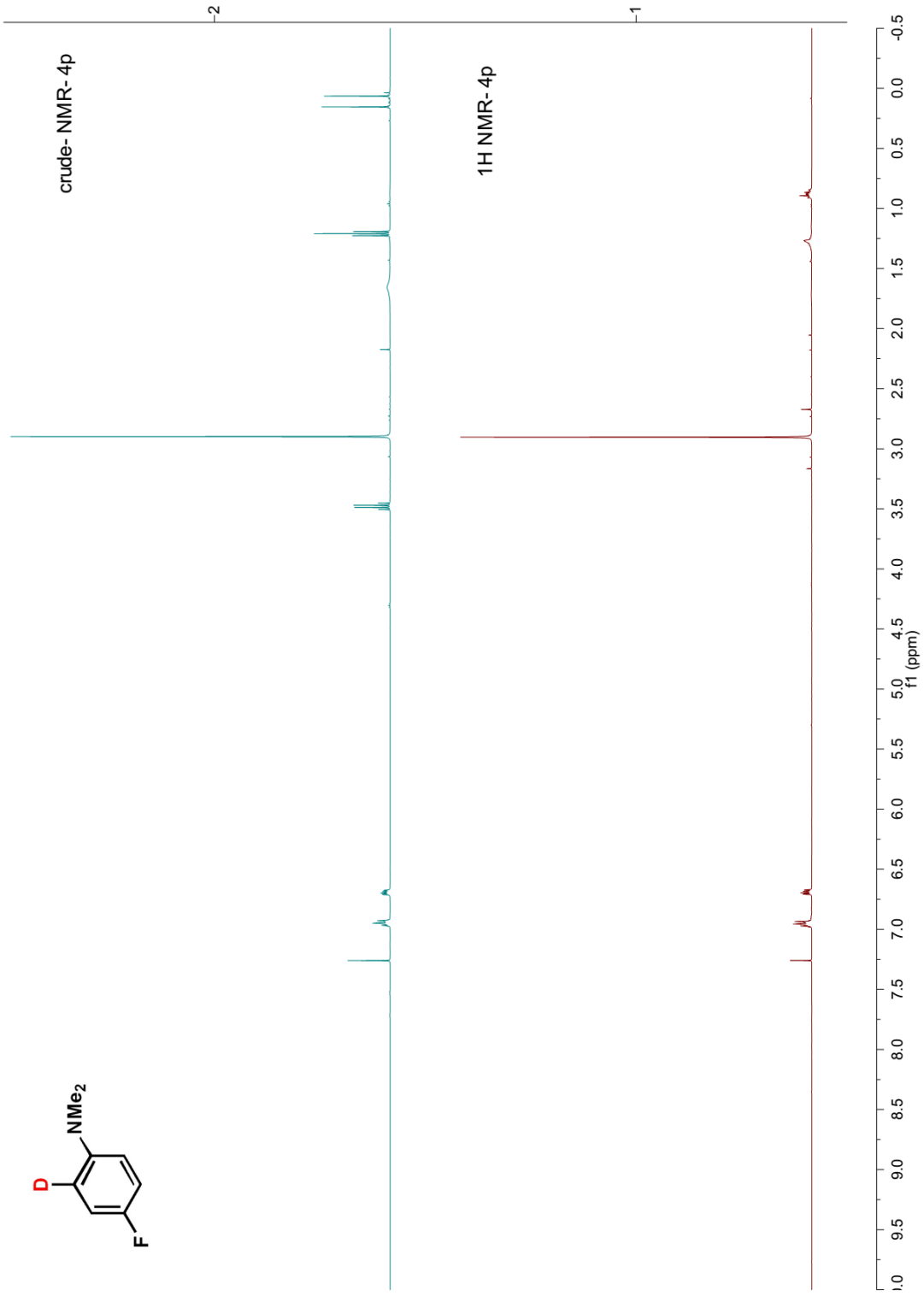

crude NMR- 4k
1H NMR- 4k
D
D
O
O
f1 (ppm)

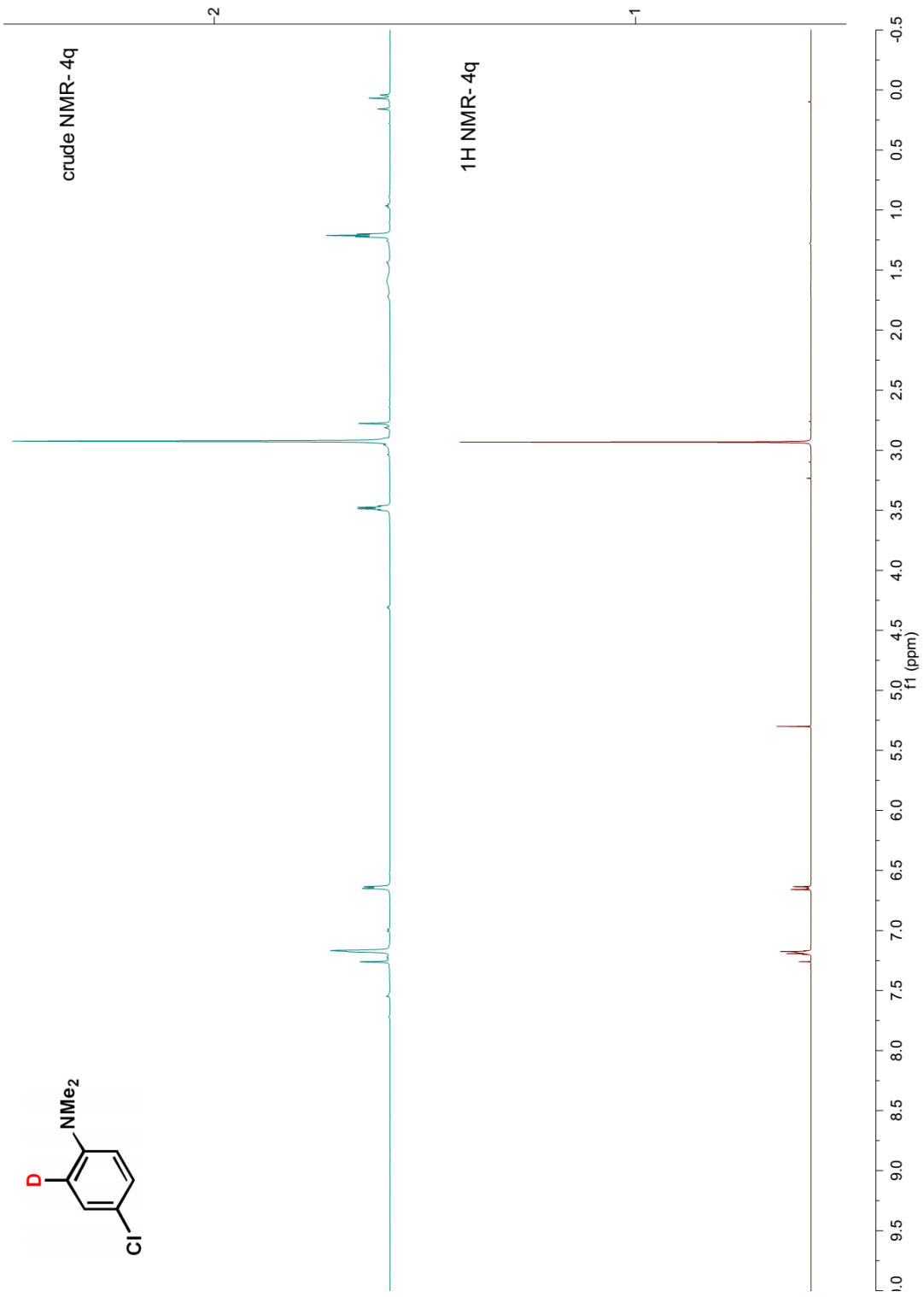

crude NMR-4l
1H NMR-4l
2
1
f1 (ppm)
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
D
S
O
O
Me

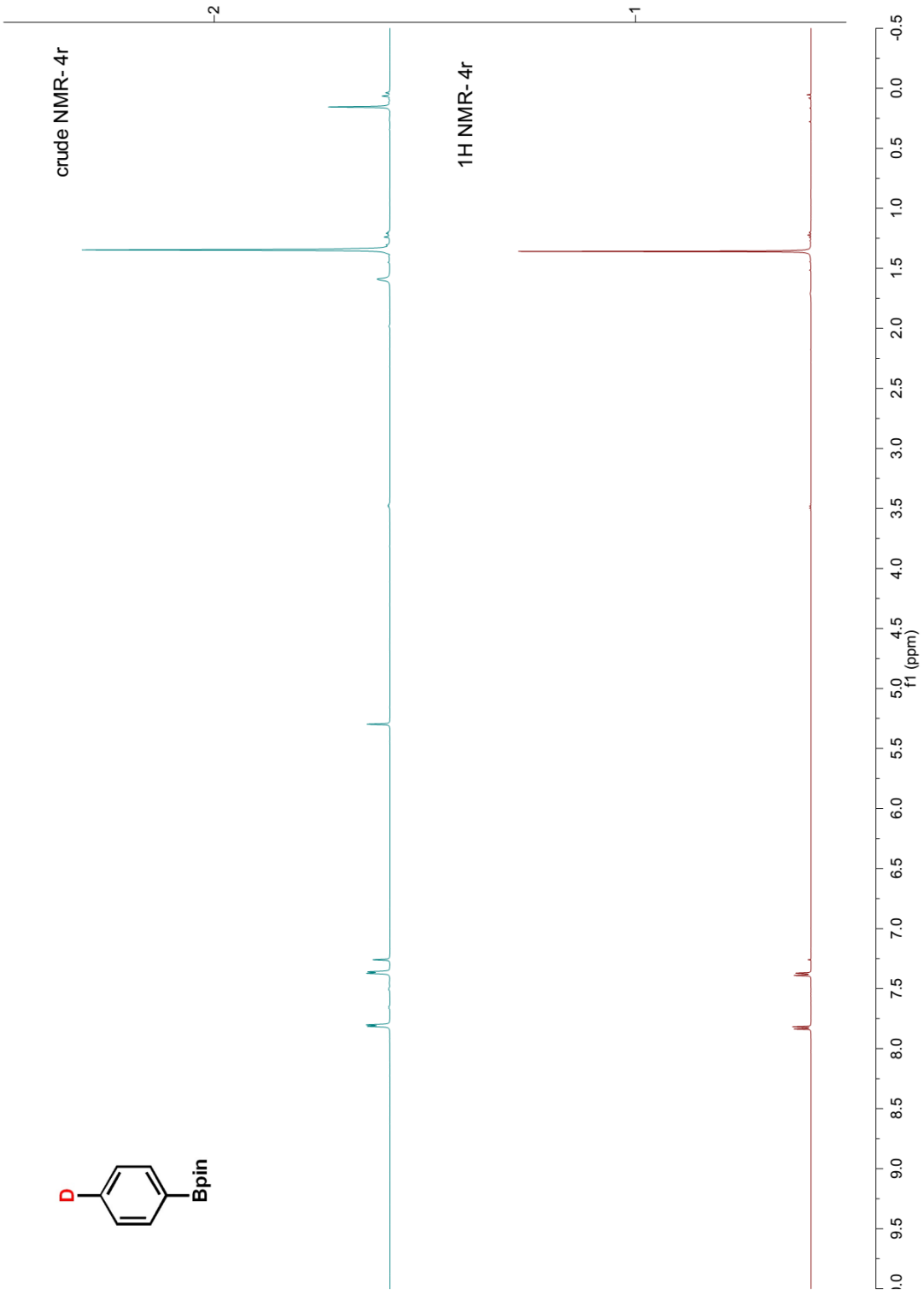

crude NMR-4m
1H NMR-4m
Et
N
Et
D
f1 (ppm)

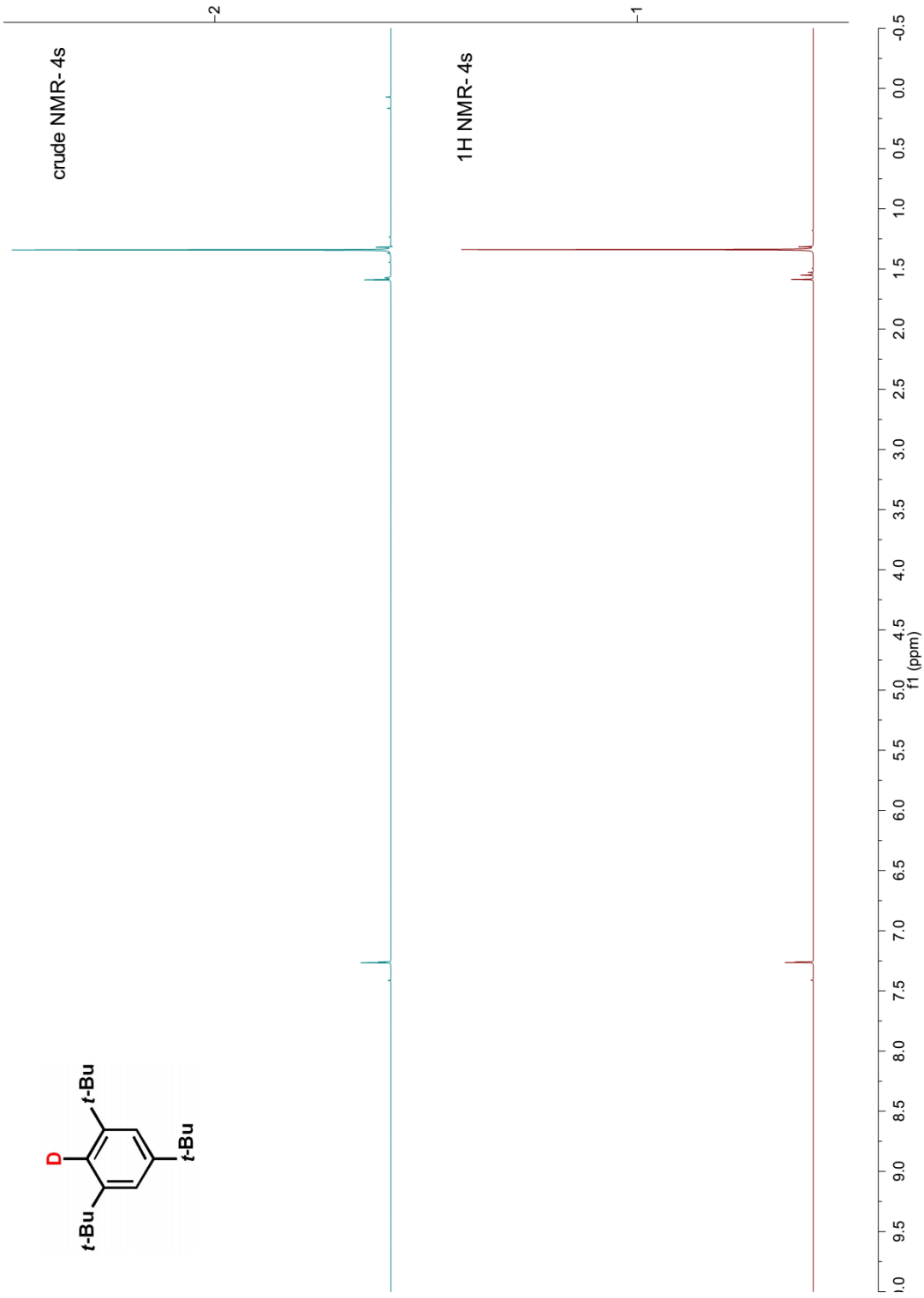

crude NMR-4n
1H NMR-4n
f1 (ppm)
O
N
D

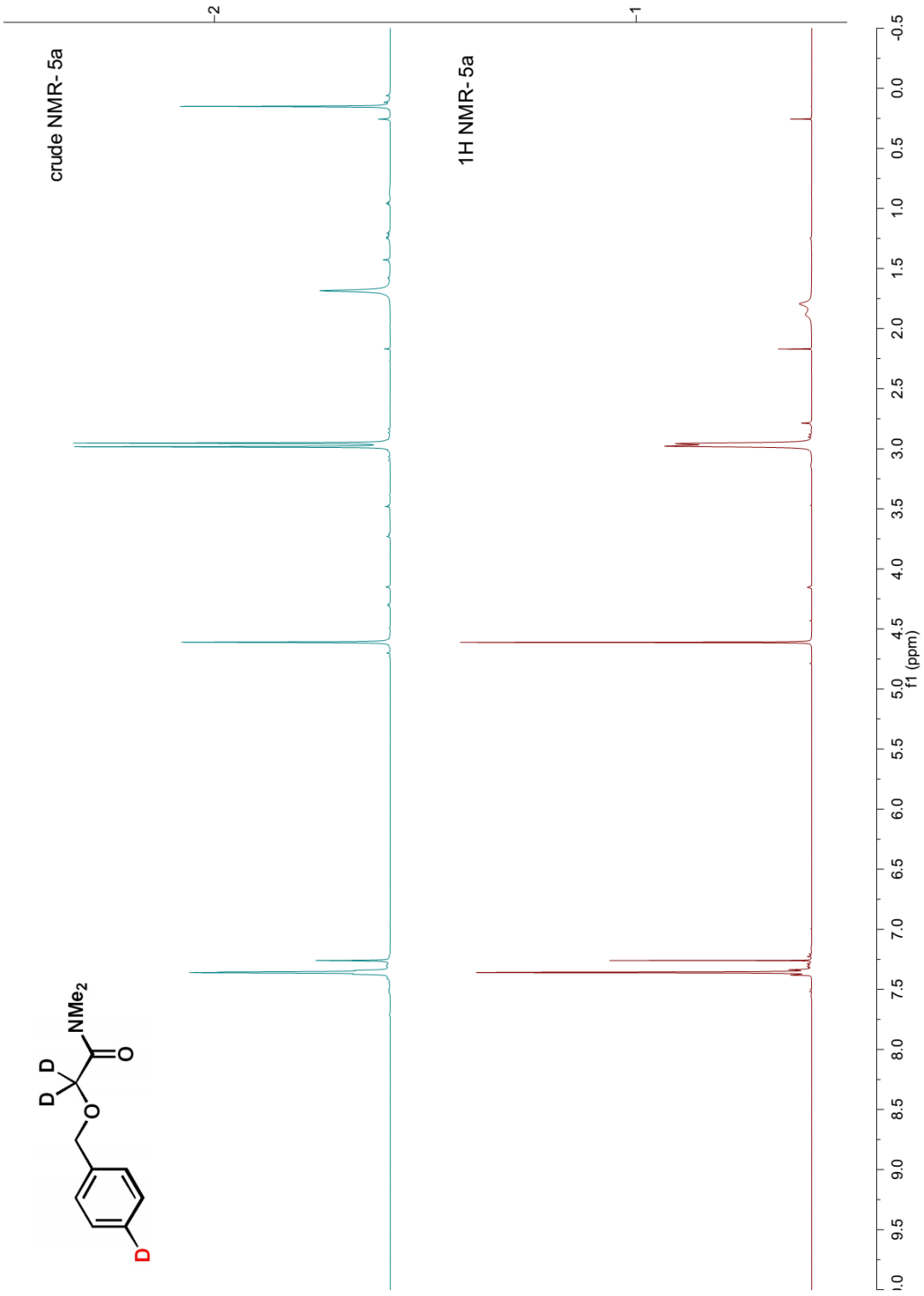

crude NMR- 4o
1H NMR- 4o
OBn
D
f1 (ppm)

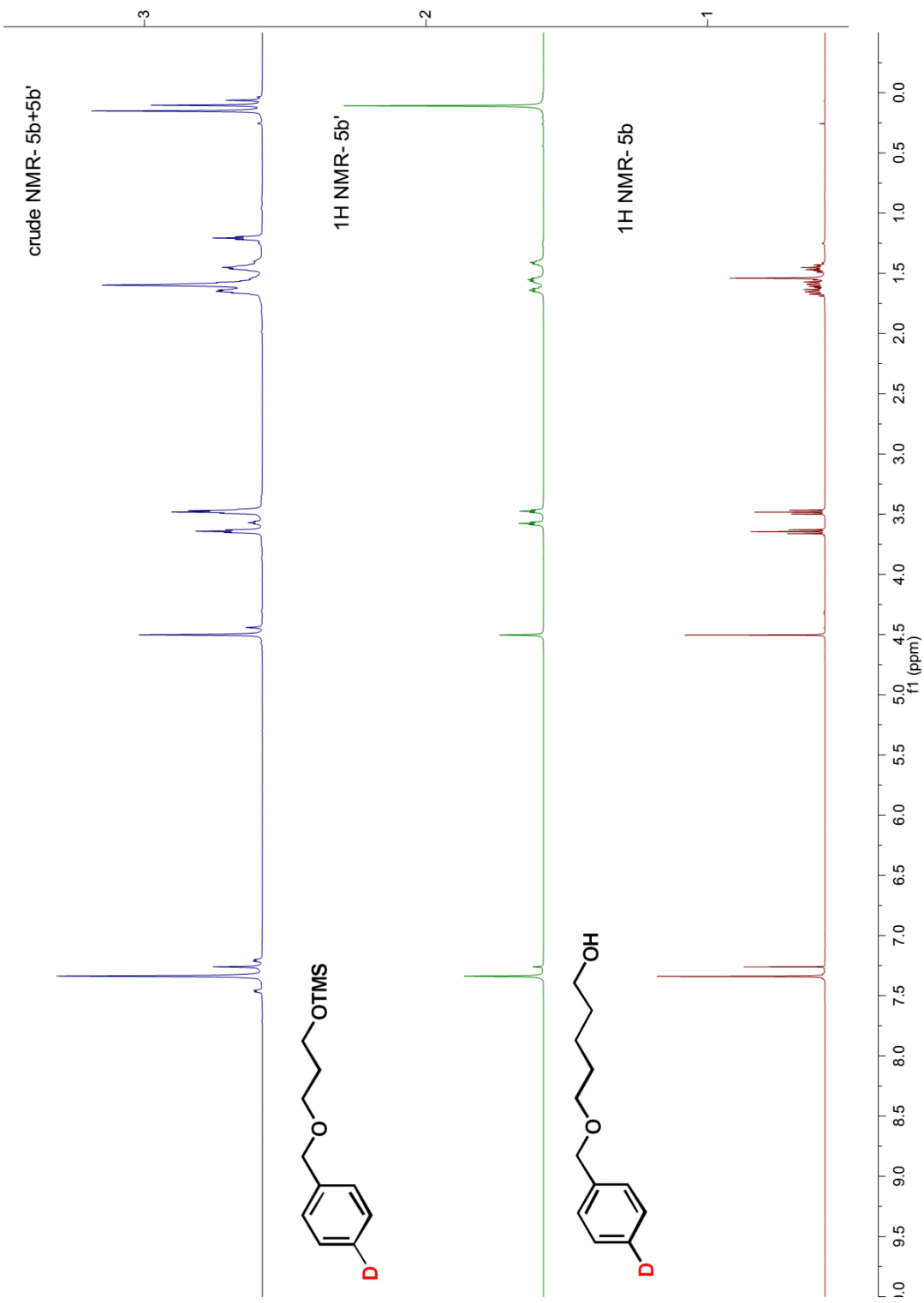

crude- NMR- 4p
1H NMR- 4p
NMe2
D
F
f1 (ppm)

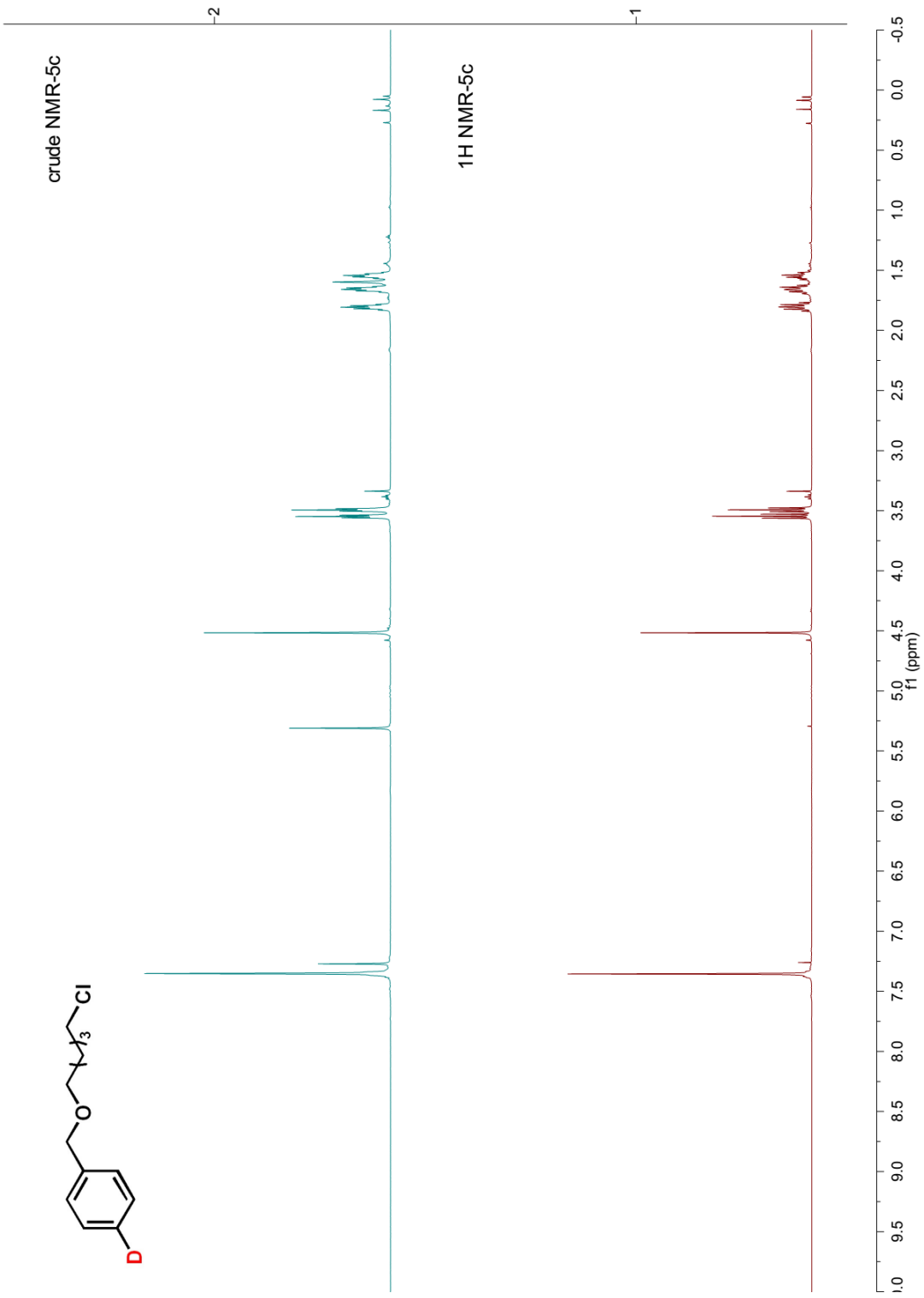

crude NMR- 4q
1H NMR- 4q
NMe2
D
Cl
f1 (ppm)

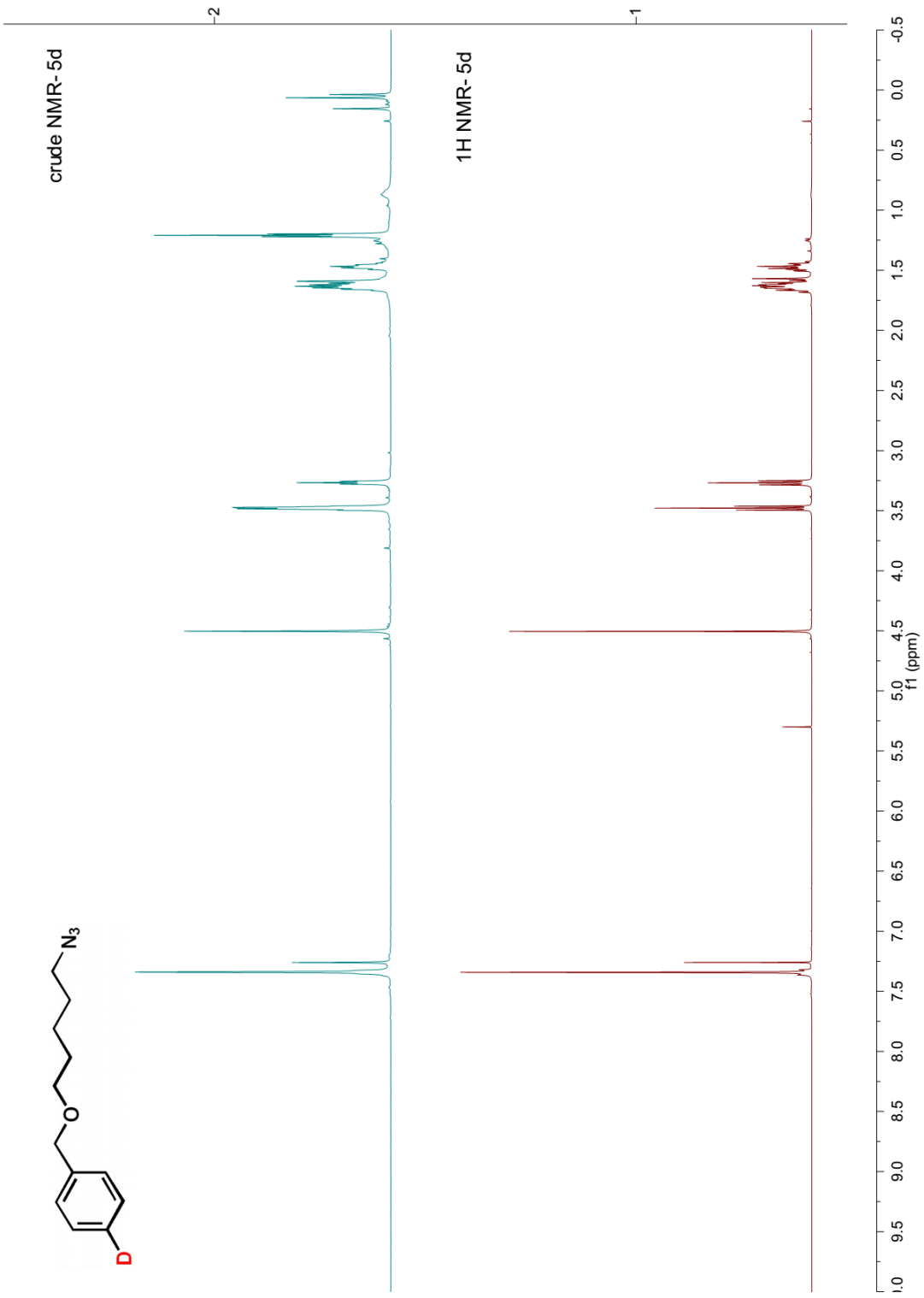

crude NMR- 4r
1H NMR- 4r
D
Bpin
f1 (ppm)

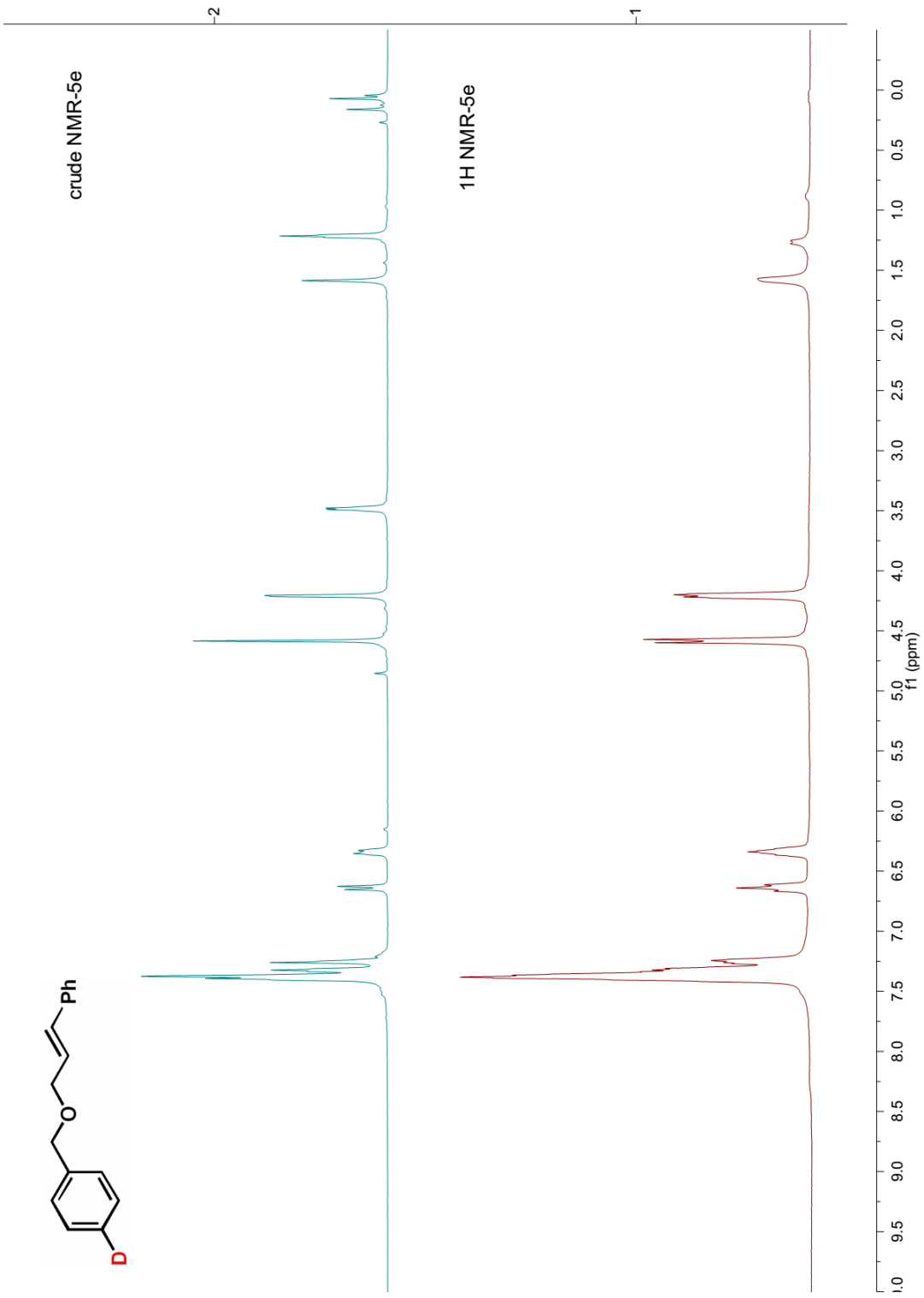

crude NMR- 4s
1H NMR- 4s
f1 (ppm)
t-Bu
t-Bu
t-Bu
D

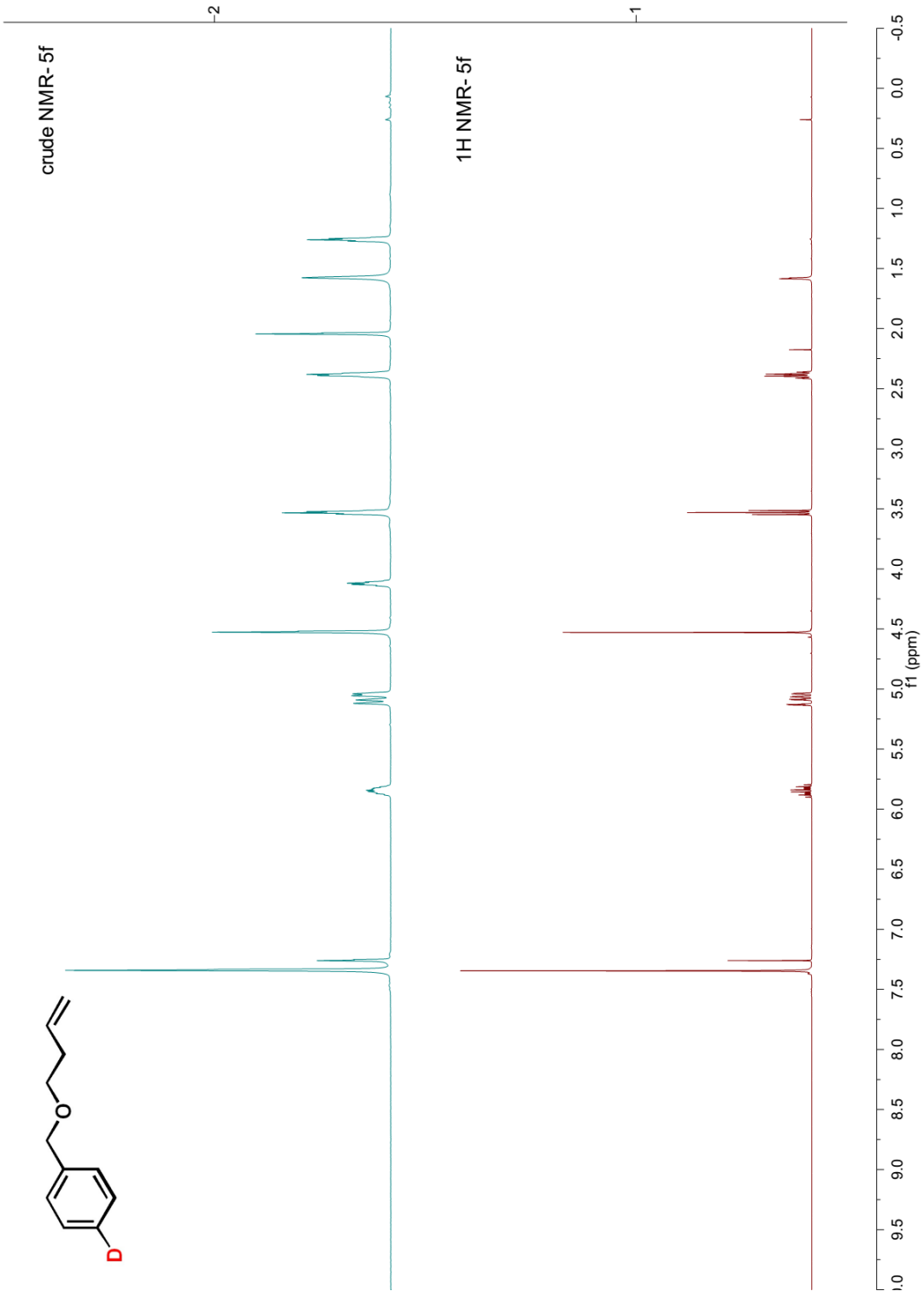

crude NMR- 5a
1H NMR- 5a
NMe2
D
D
O
O
D
f1 (ppm)

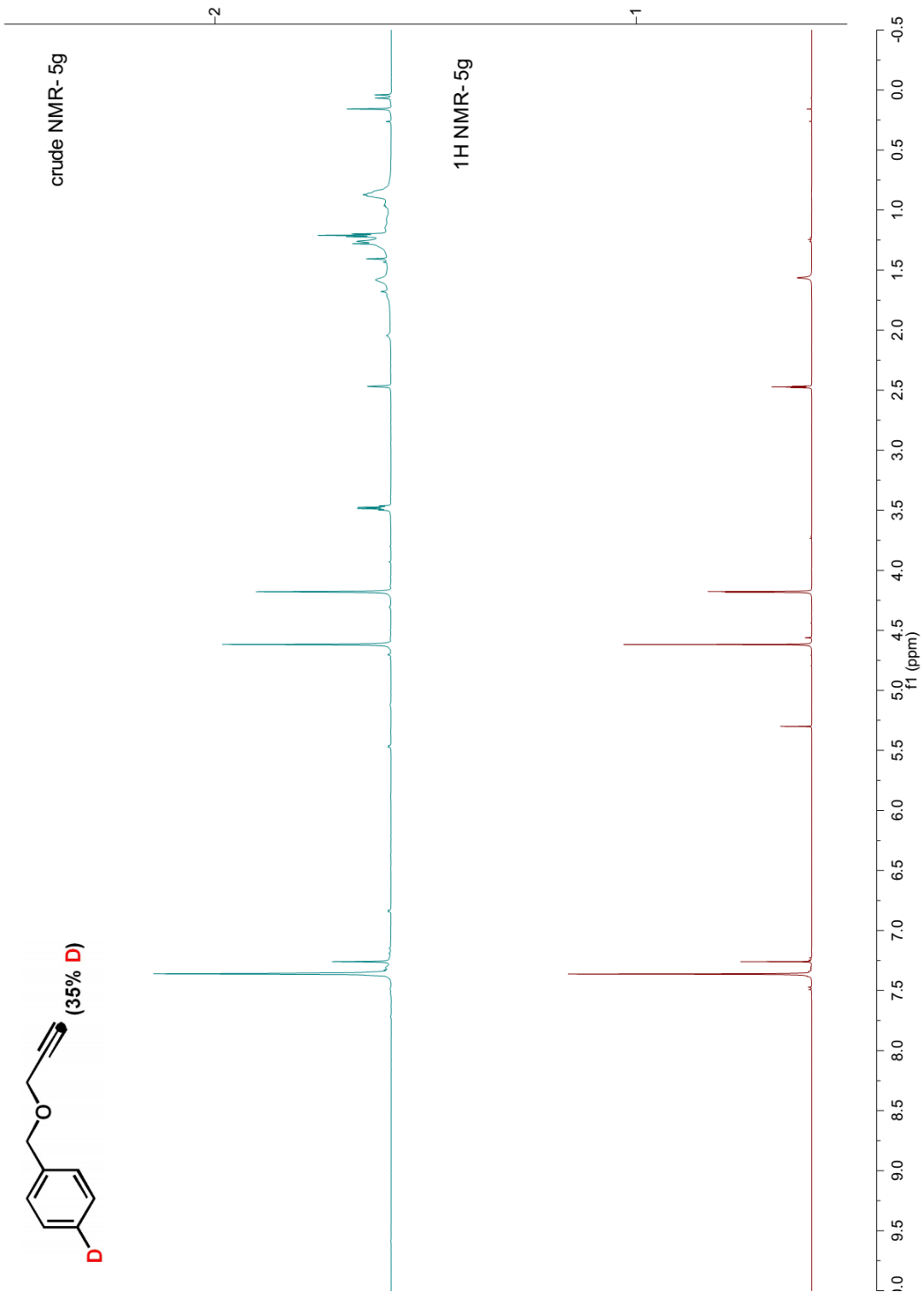

crude NMR- 5b+5b'
1H NMR- 5b'
1H NMR- 5b
OTMS
OH
O
O
D
D
f1 (ppm)

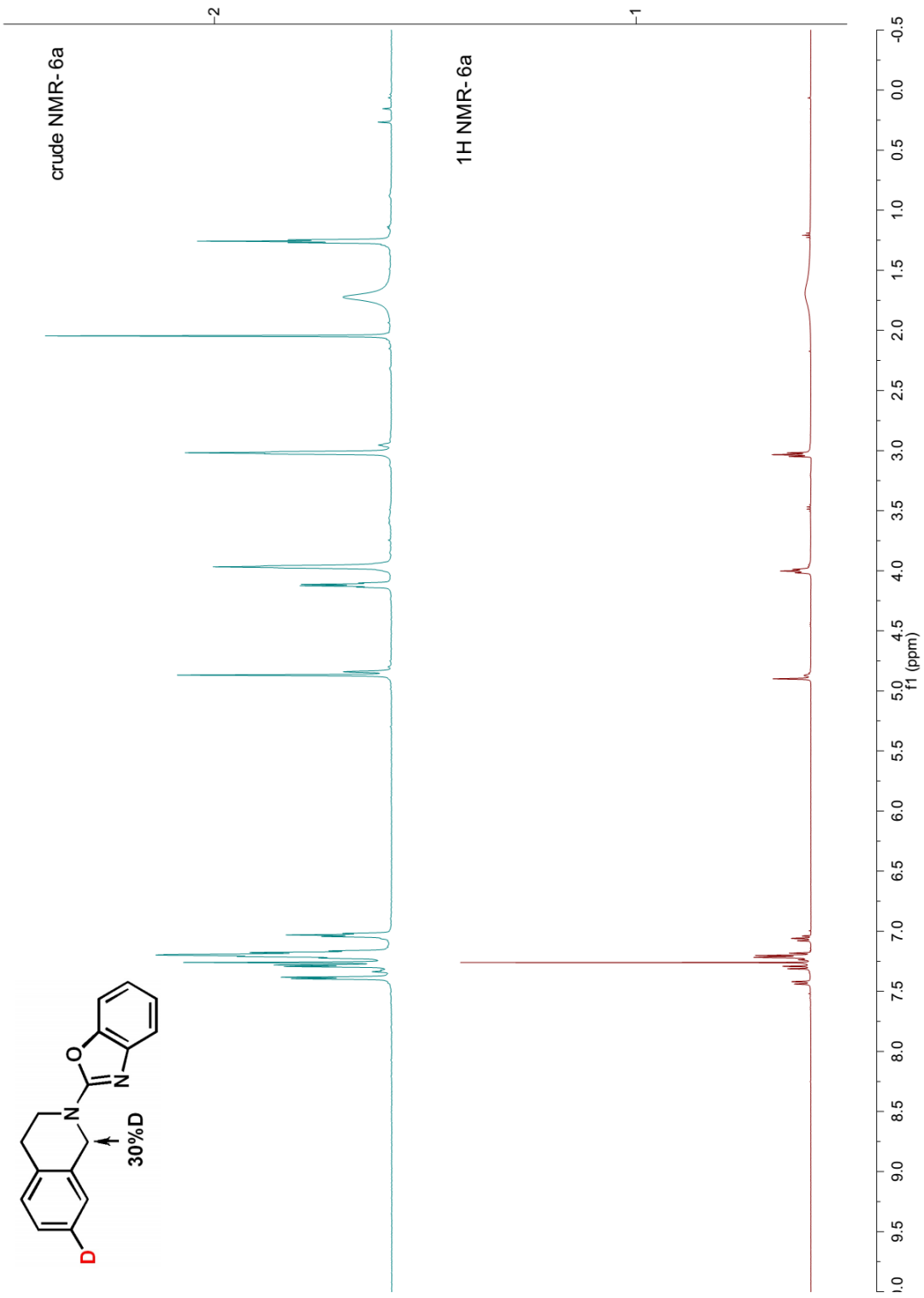

crude NMR-5c
1H NMR-5c
D
O
3
Cl
f1 (ppm)

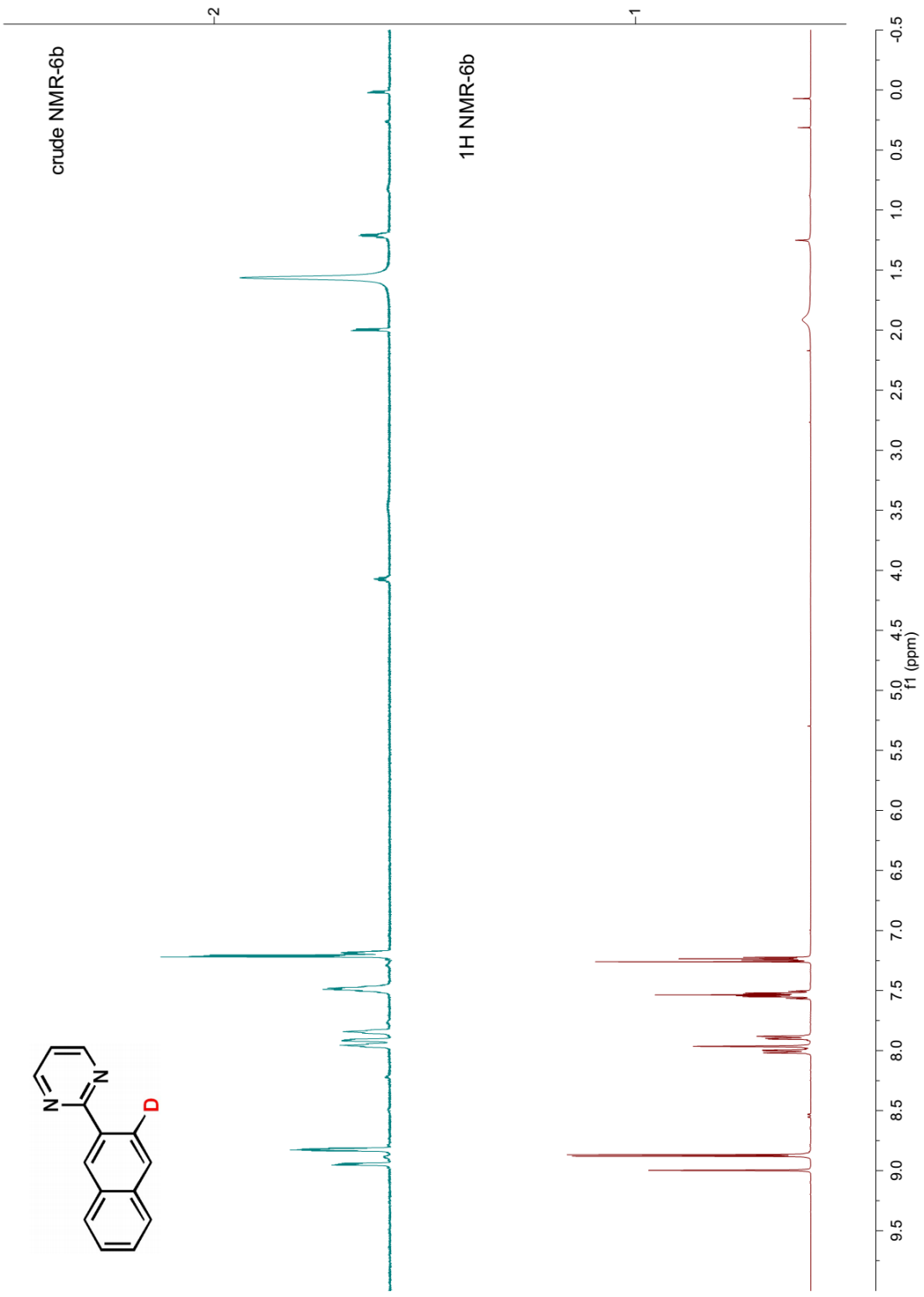

crude NMR- 5d
1H NMR- 5d
N3
O
D
f1 (ppm)

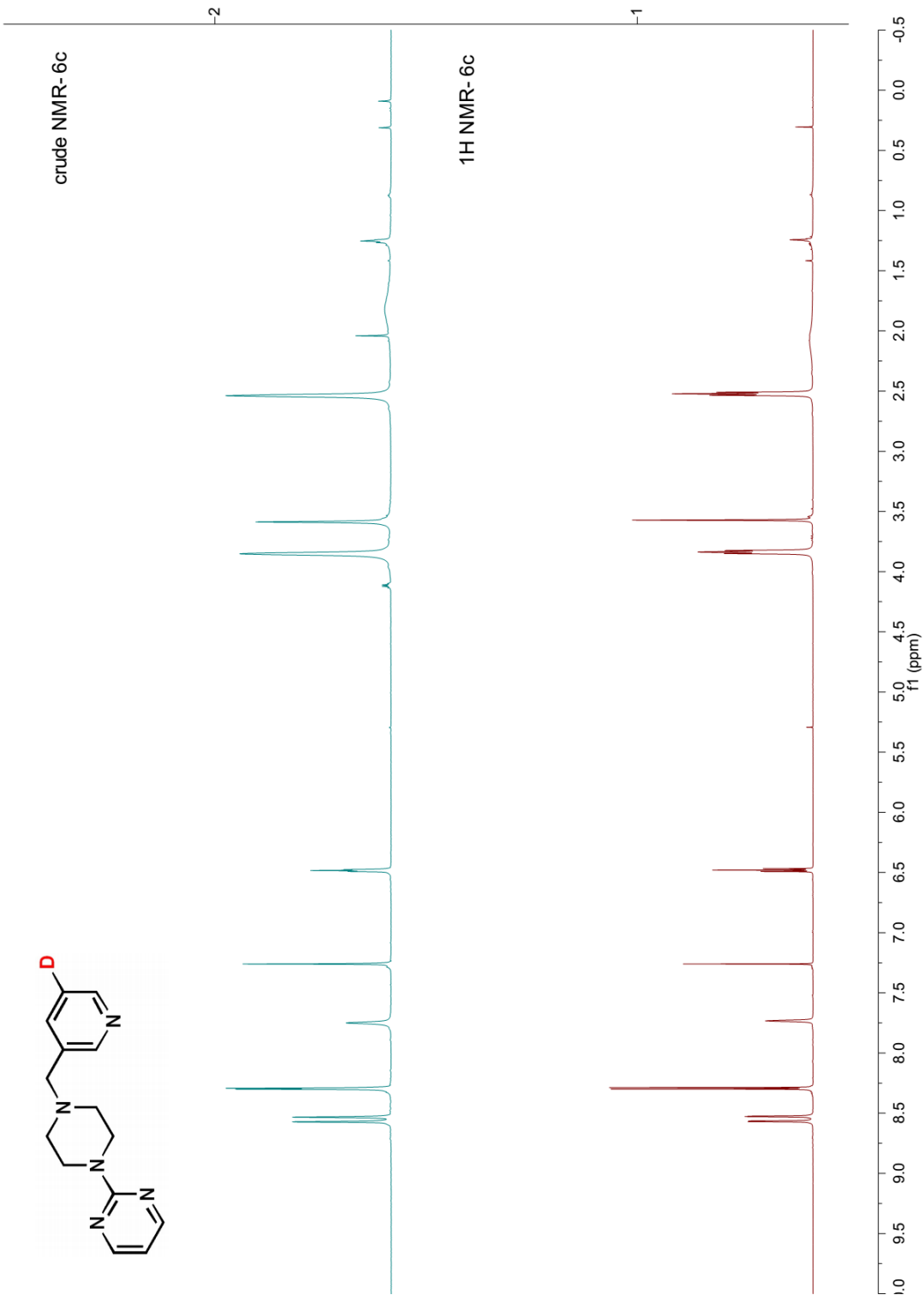

crude NMR-5e
1H NMR-5e
Ph
O
D
f1 (ppm)

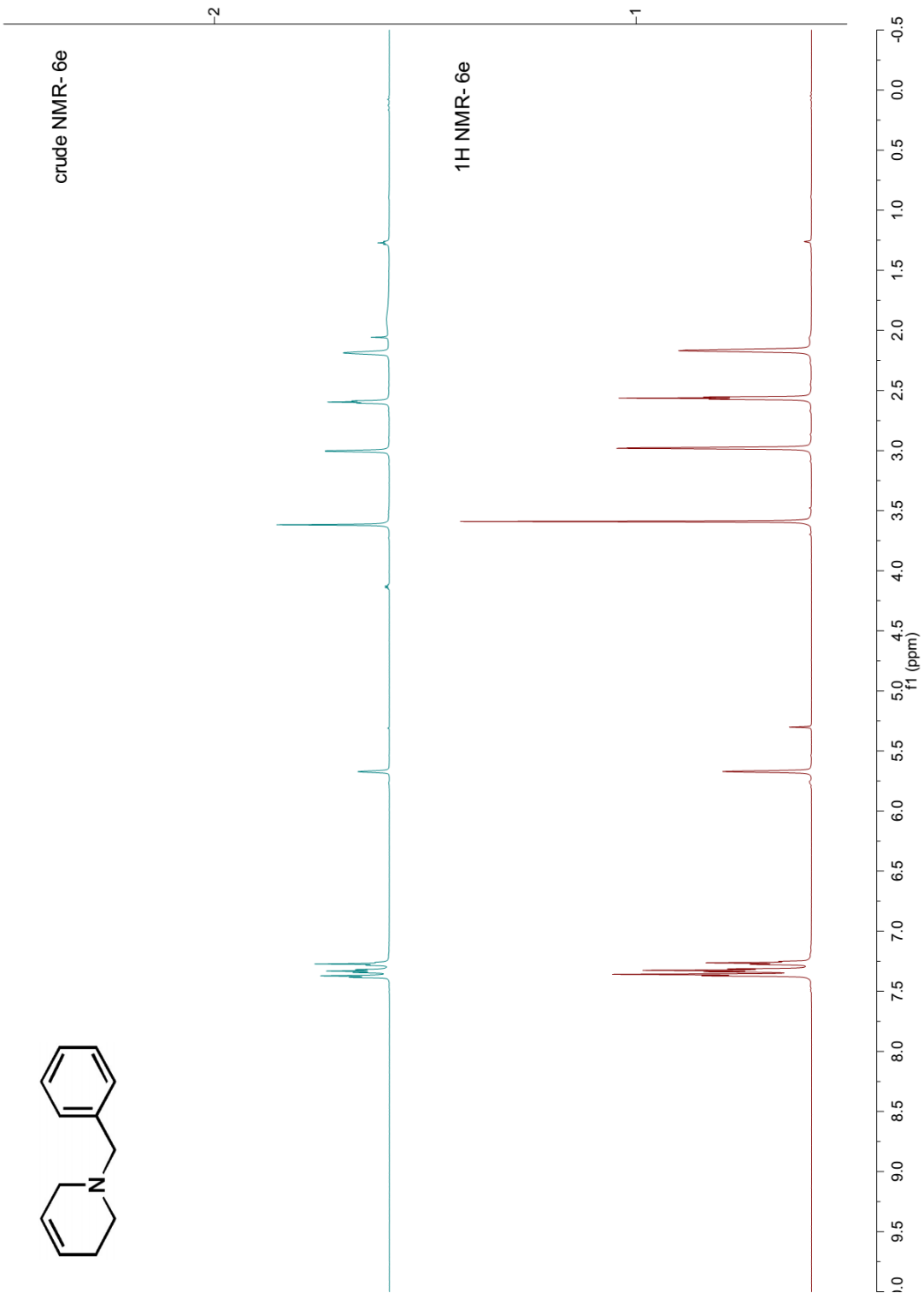

crude NMR- 5f
1H NMR- 5f
O
D
f1 (ppm)

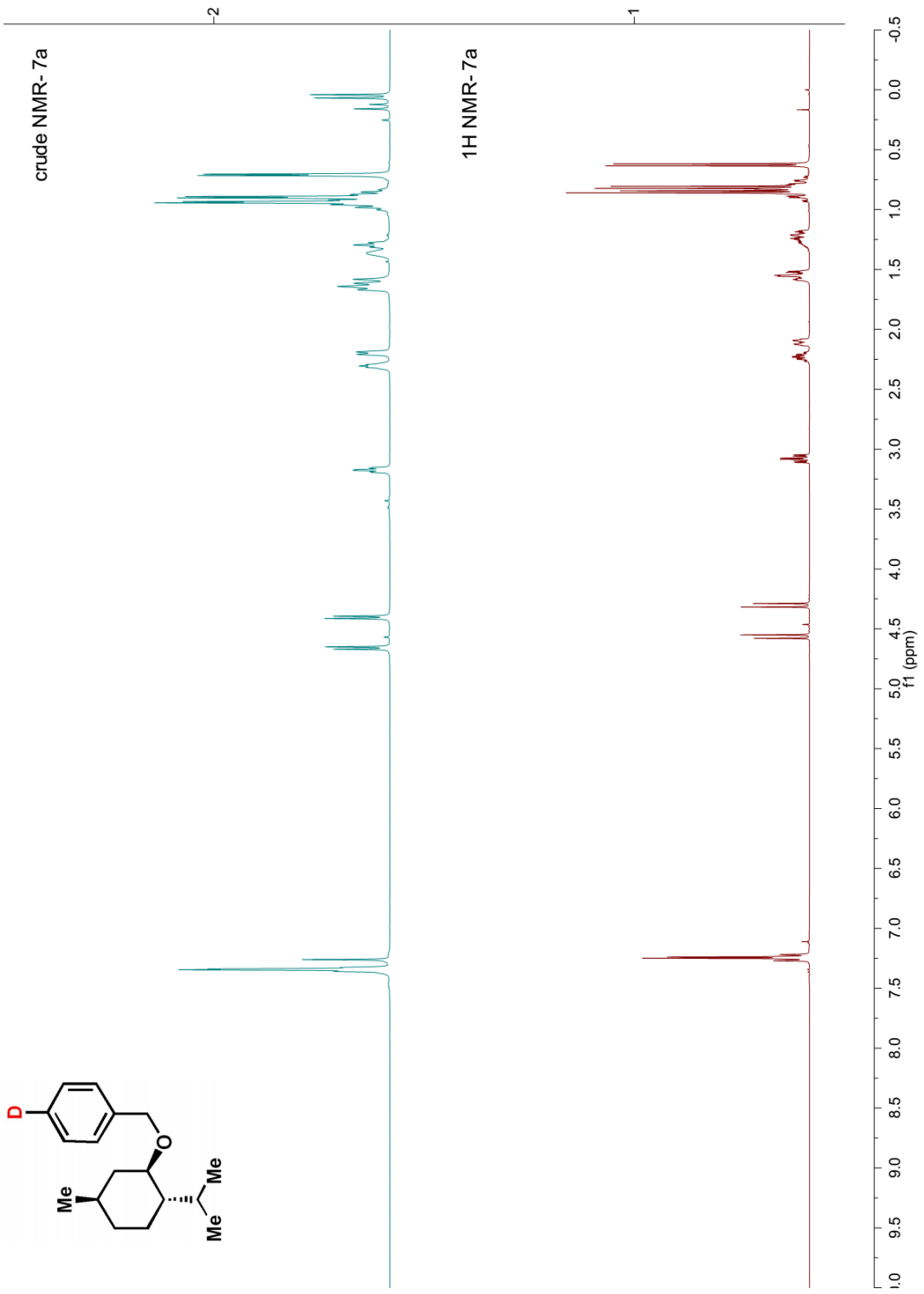

crude NMR- 5g
1H NMR- 5g
(35% D)
D
O
f1 (ppm)

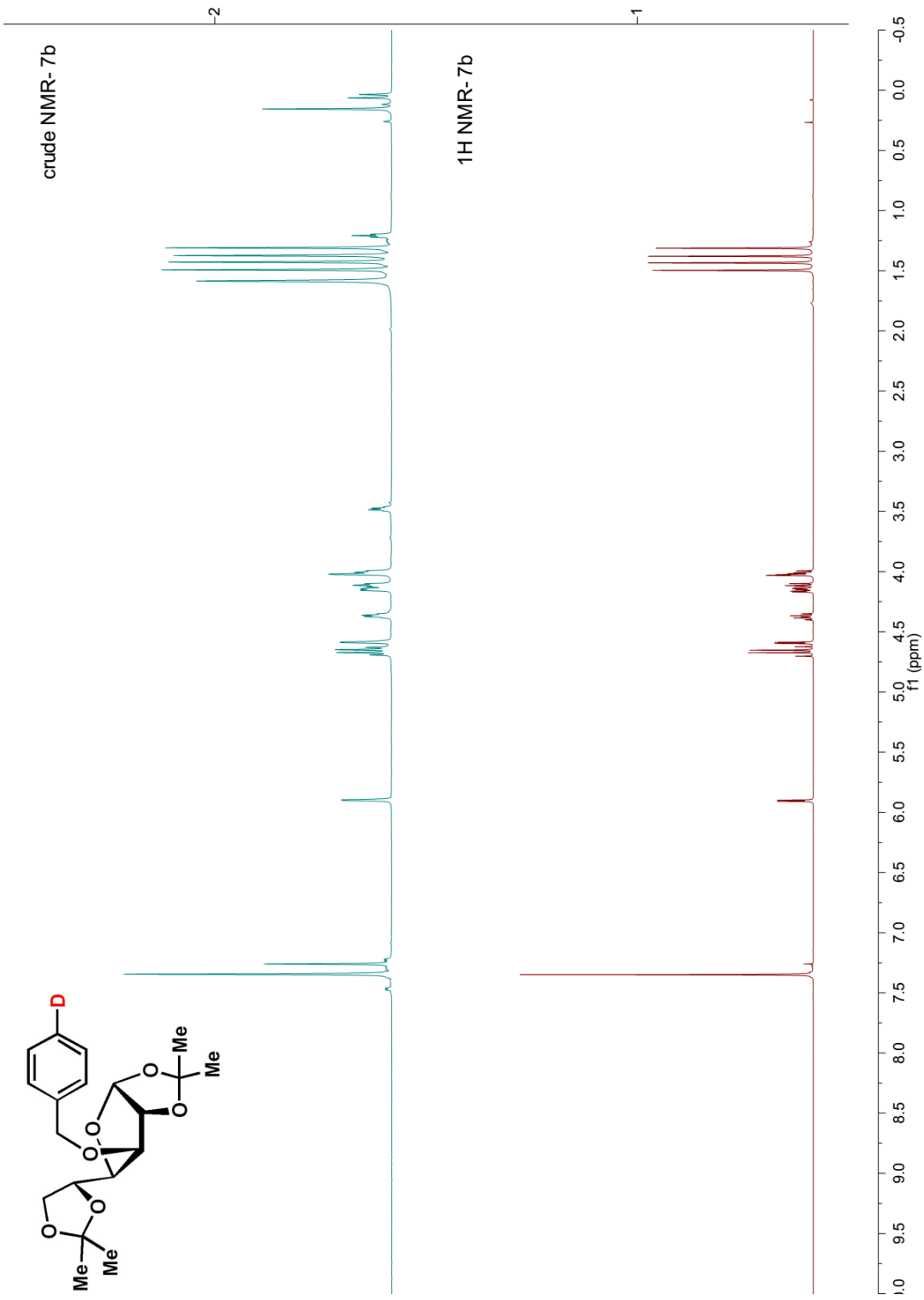

crude NMR-6a
1H NMR-6a
30%D
D
O
N
N
f1 (ppm)

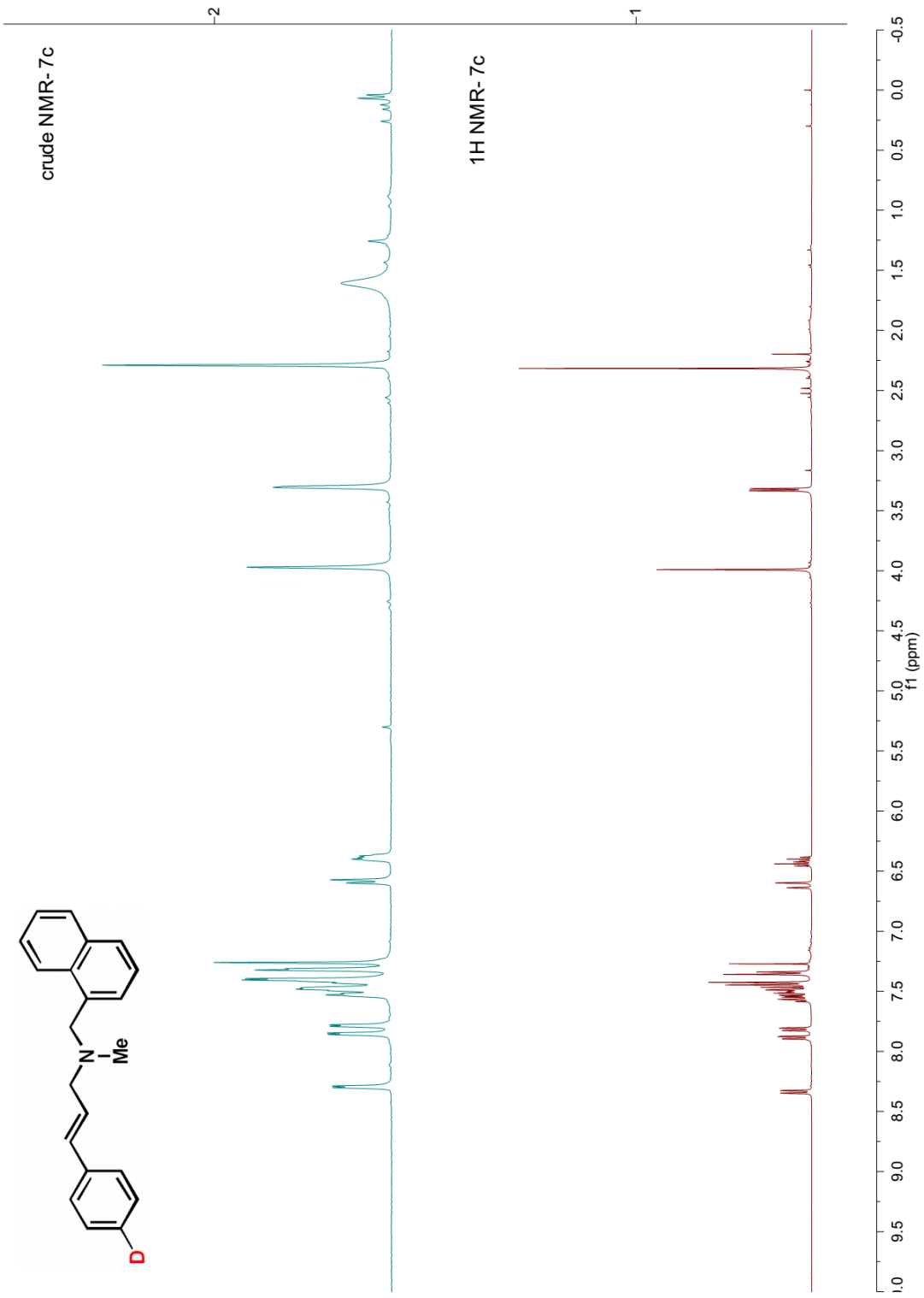

crude NMR-6b
1H NMR-6b
N
N
D
f1 (ppm)

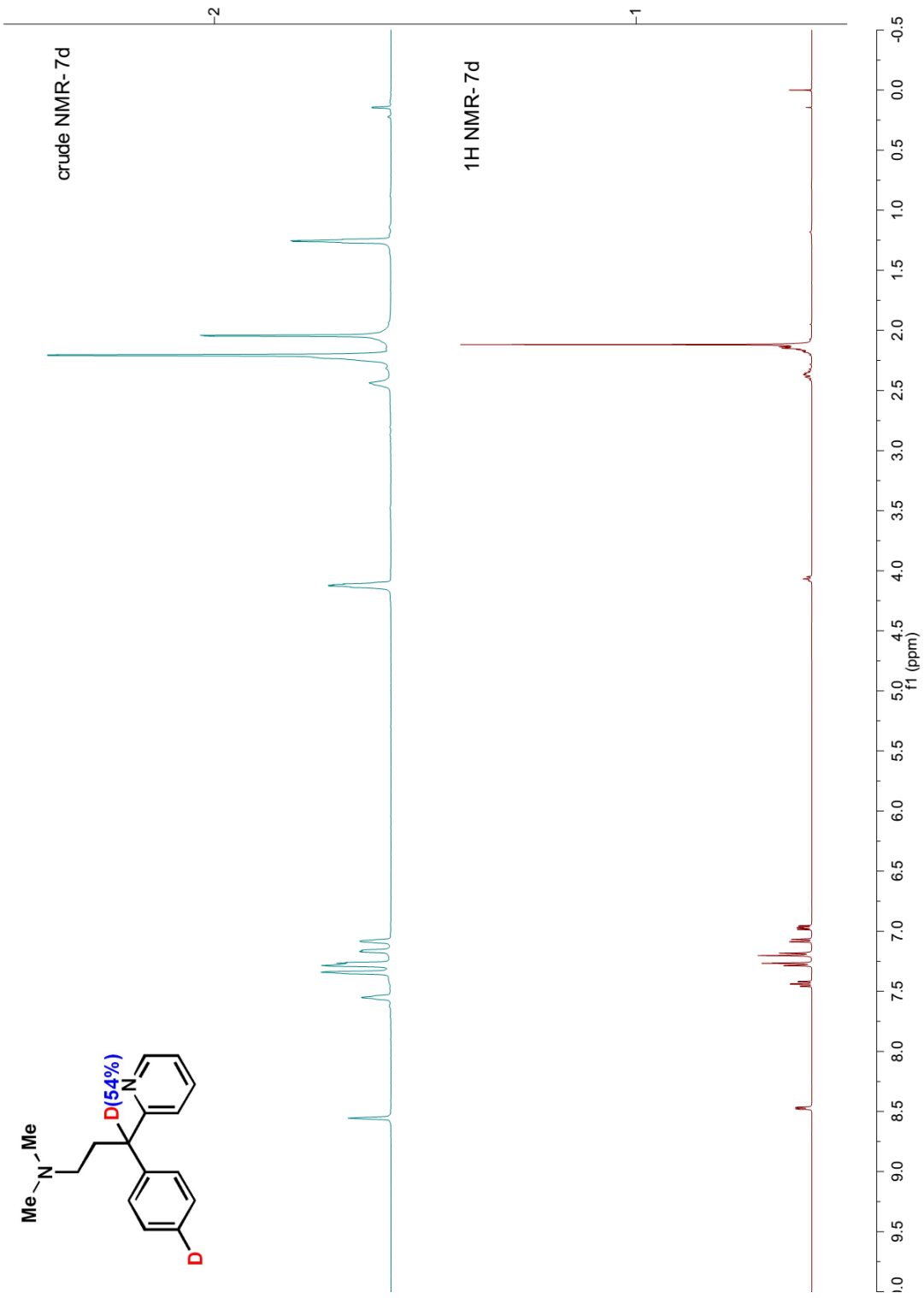

crude NMR- 6c
1H NMR- 6c
D
N
N
N
N
N
2
1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
f1 (ppm)

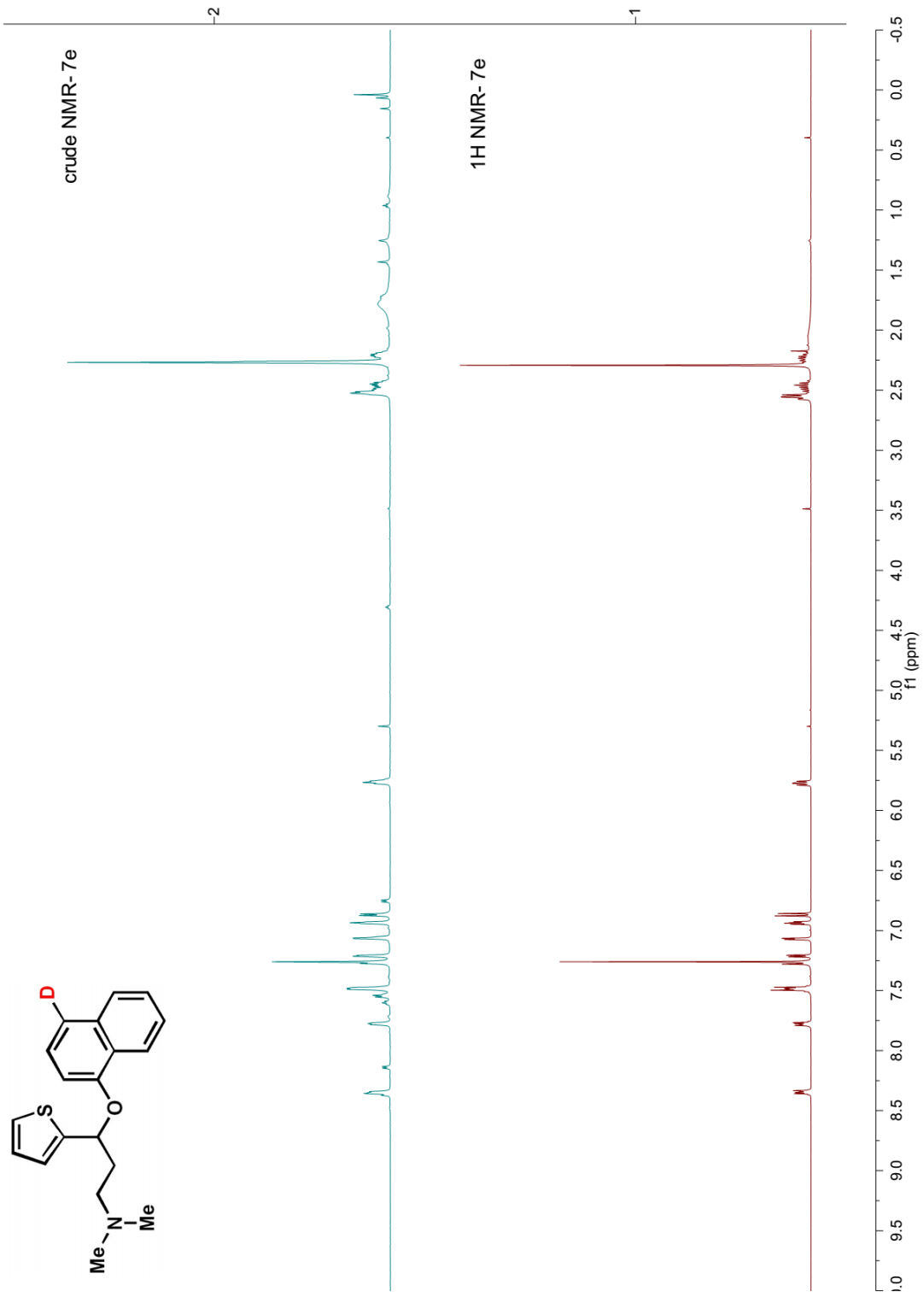

crude NMR- 6e
1H NMR- 6e
N
f1 (ppm)

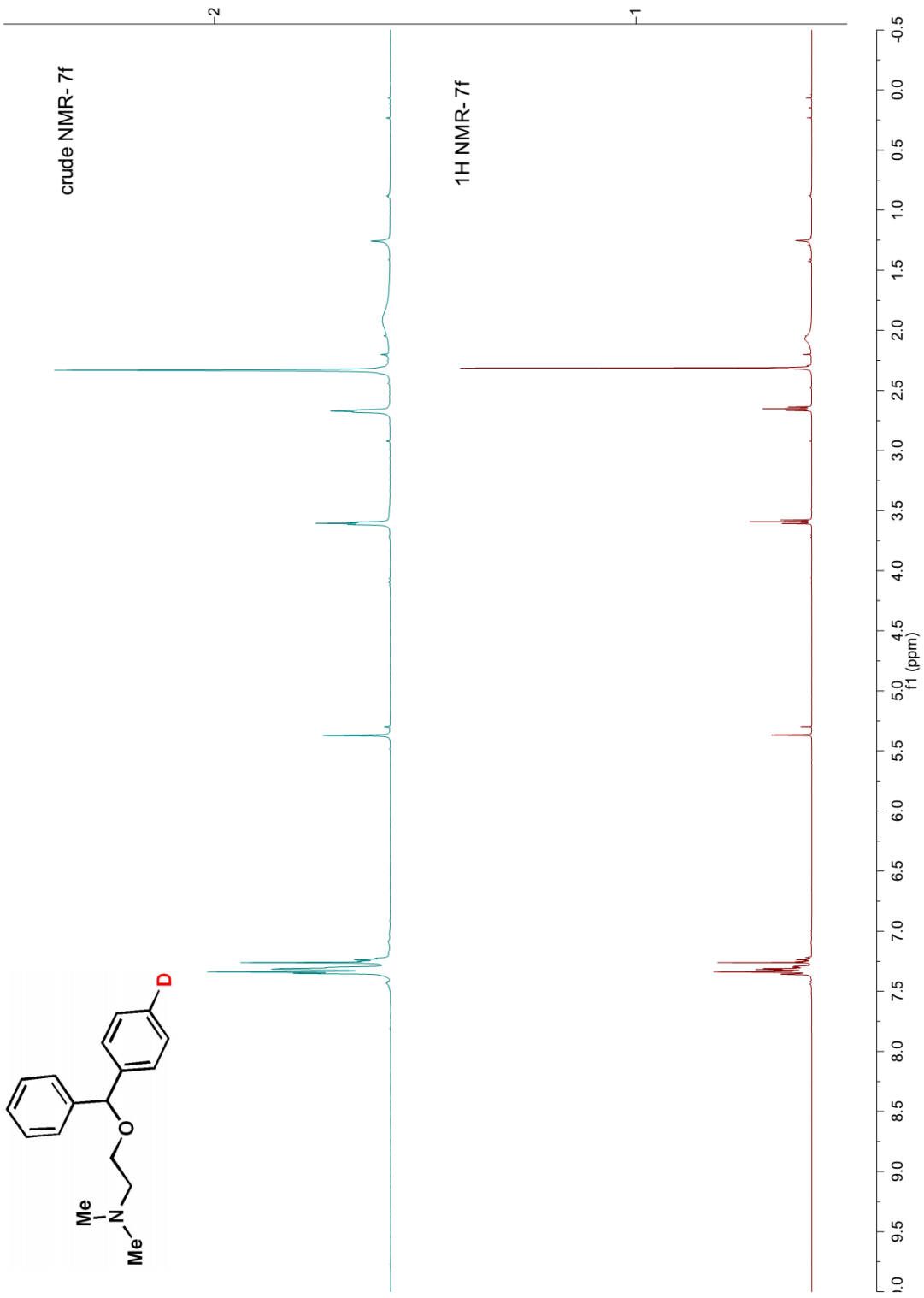

crude NMR- 7a
1H NMR- 7a
D
O
Me
Me
Me
f1 (ppm)

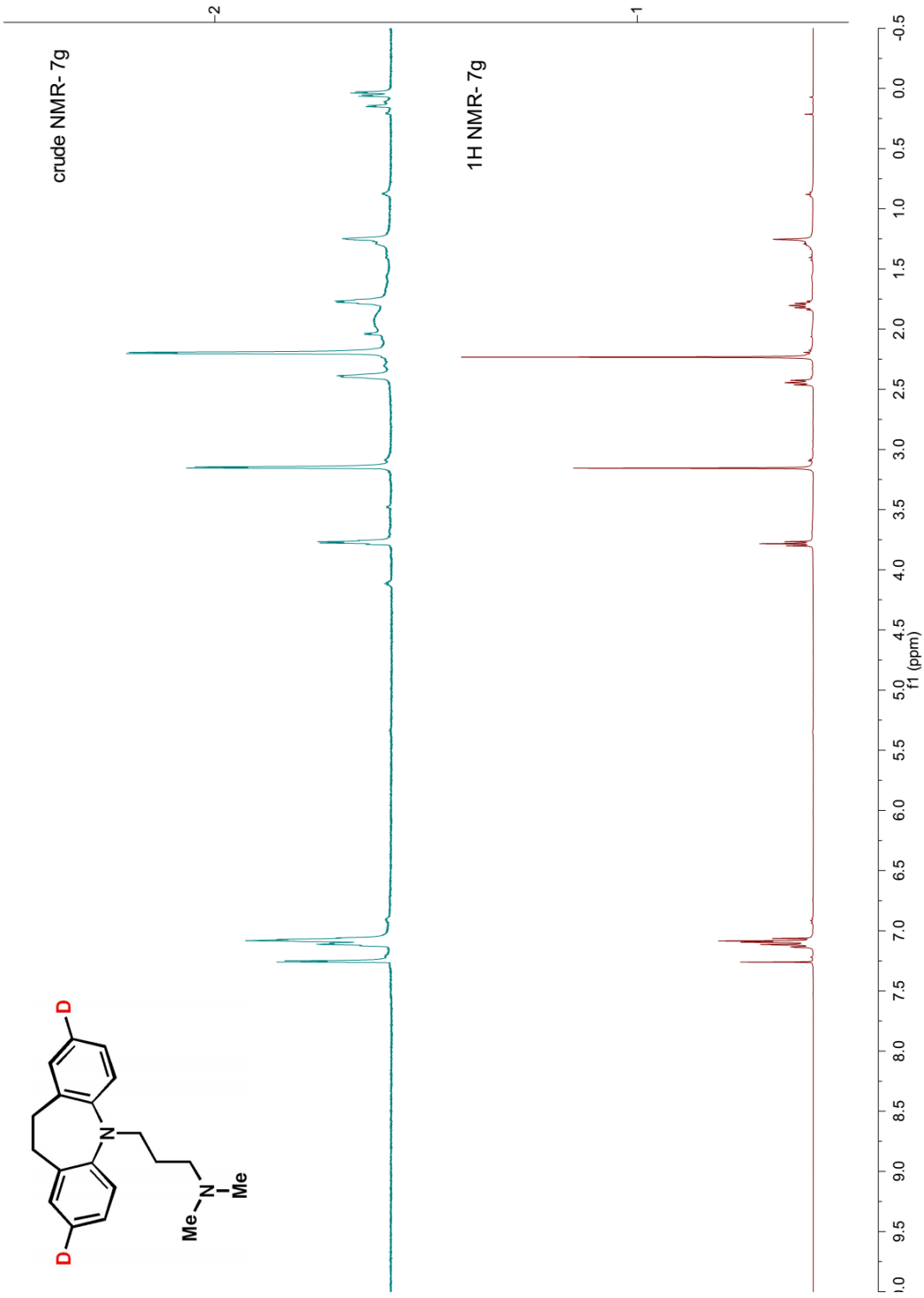

crude NMR- 7b
1H NMR- 7b
f1 (ppm)
D
Me
Me
Me
Me

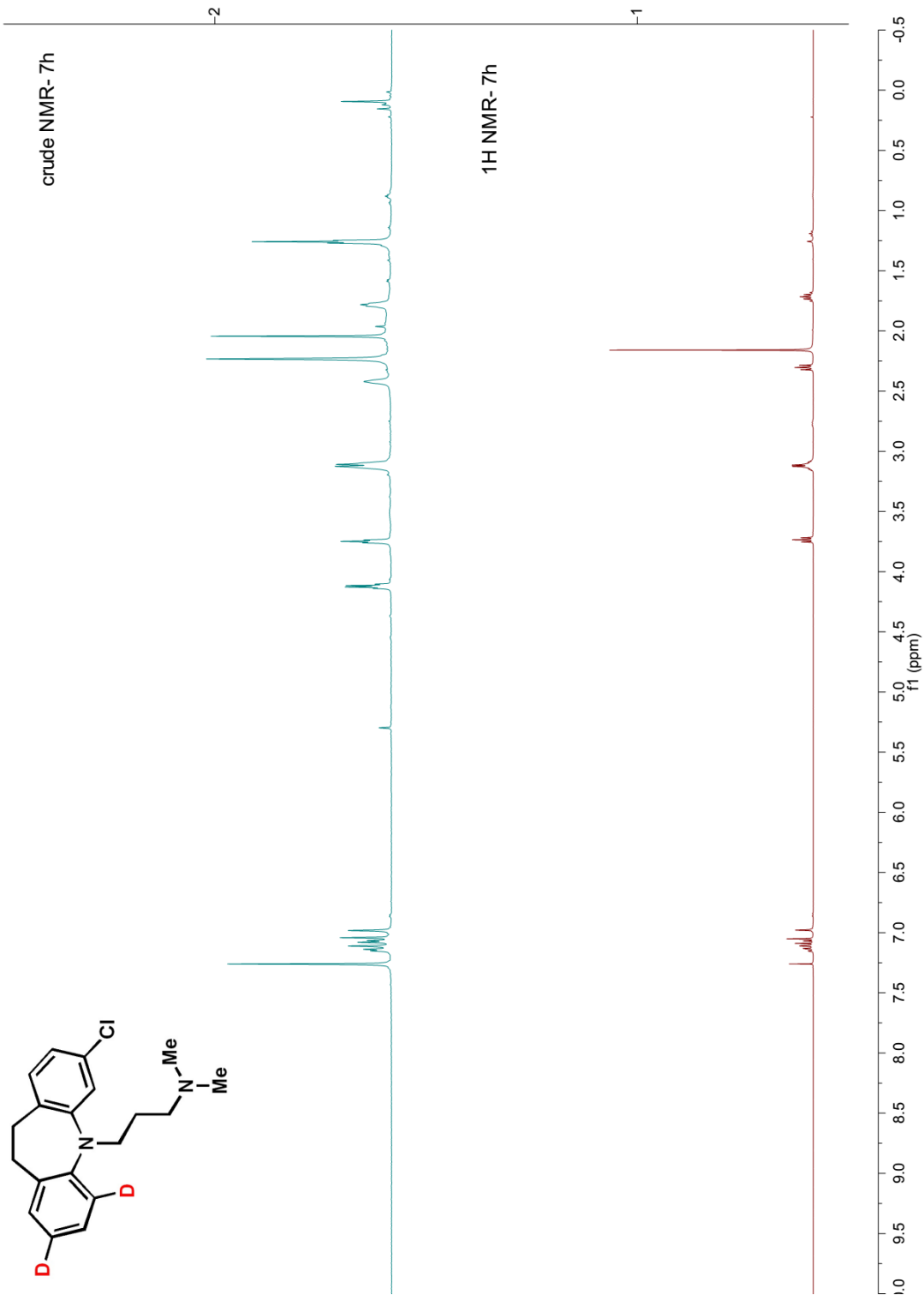

crude NMR- 7c
1H NMR- 7c
N
Me
D
f1 (ppm)

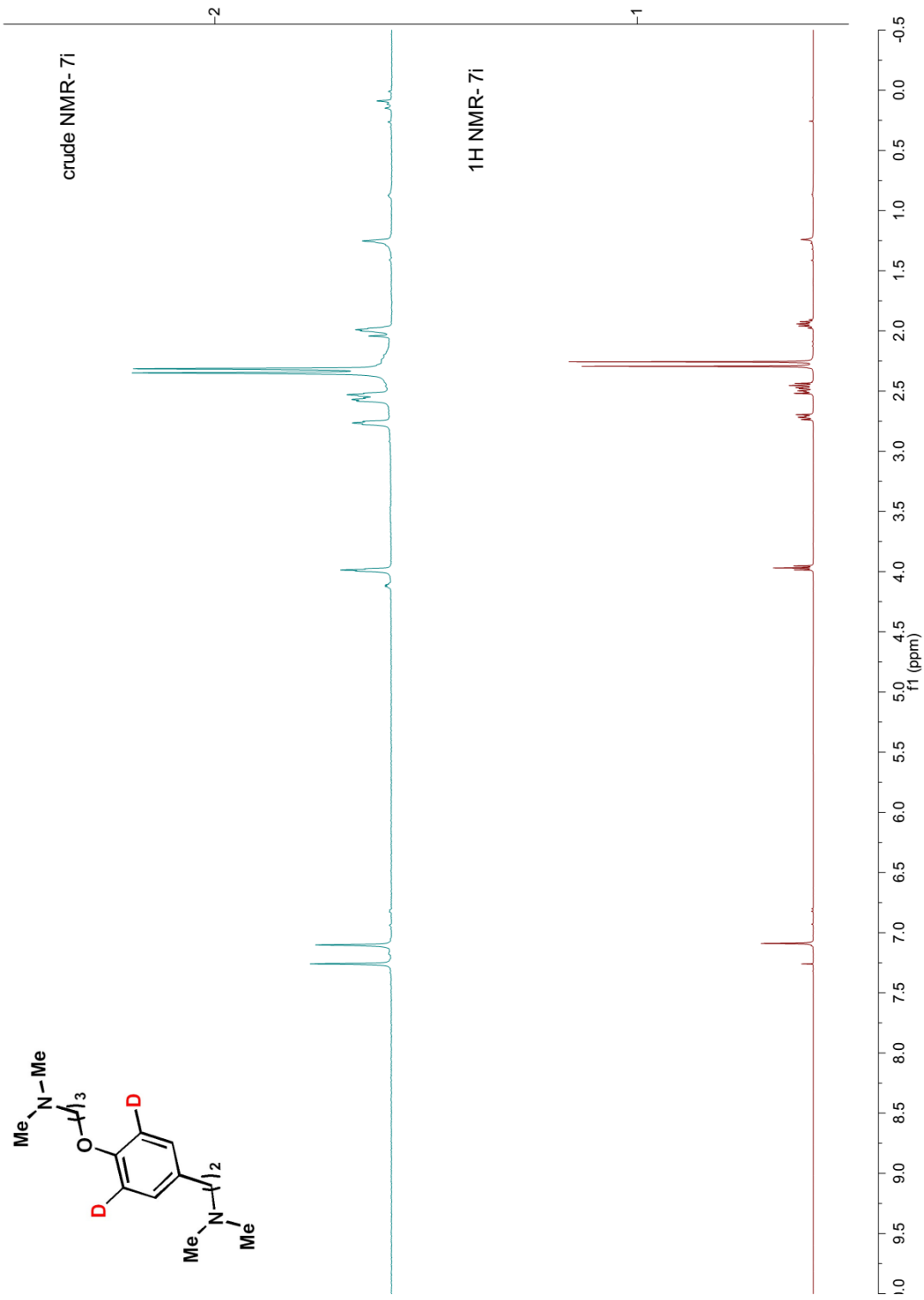

crude NMR- 7d
1H NMR- 7d
Me
N
Me
D(54%)
N
D
f1 (ppm)

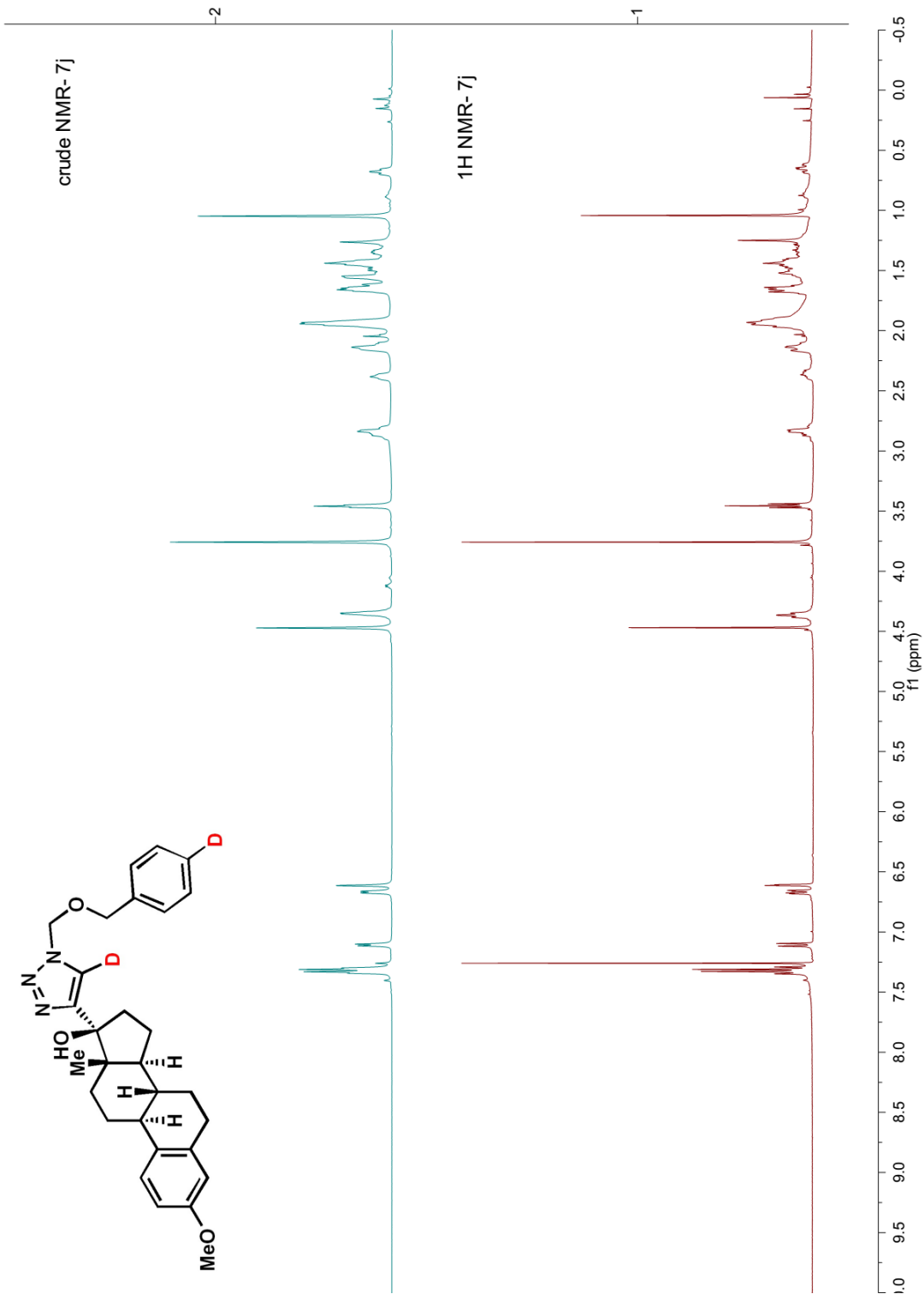

crude NMR- 7e
1H NMR- 7e
D
S
O
N
Me
Me
f1 (ppm)

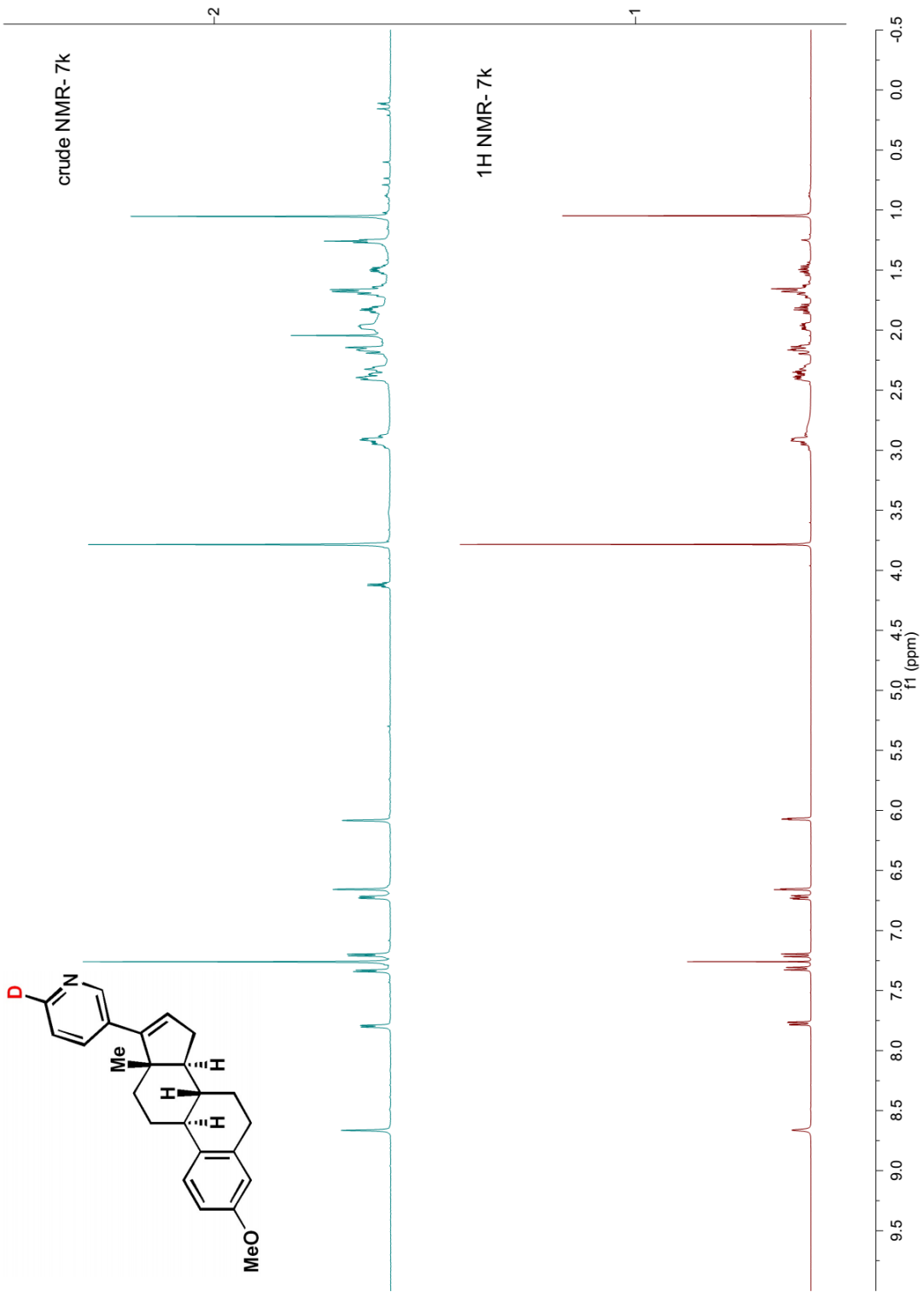

crude NMR- 7f
1H NMR- 7f
D
O
N
Me
Me
f1 (ppm)

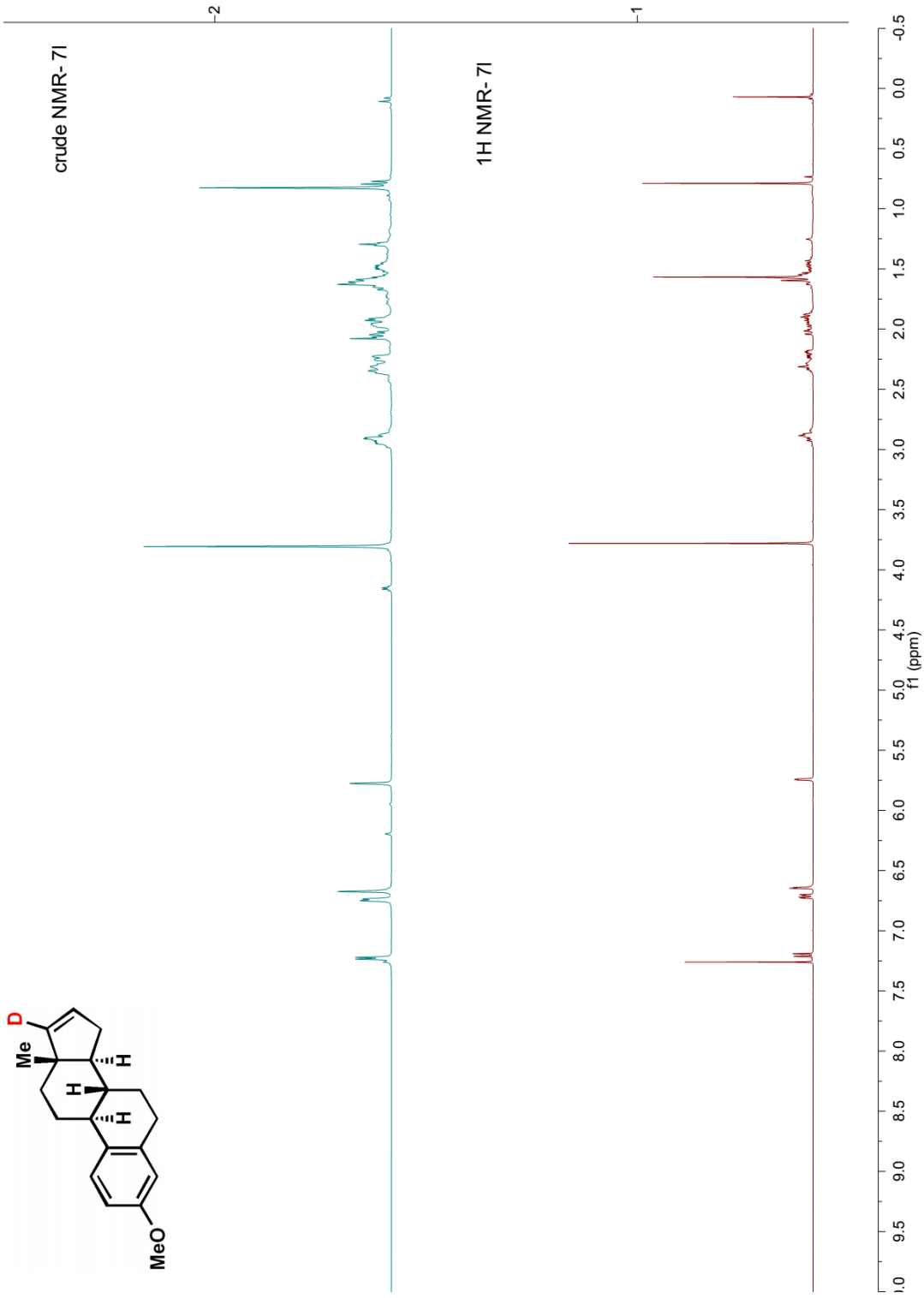

crude NMR- 7g
1H NMR- 7g
D
D
N
N
Me
Me
f1 (ppm)

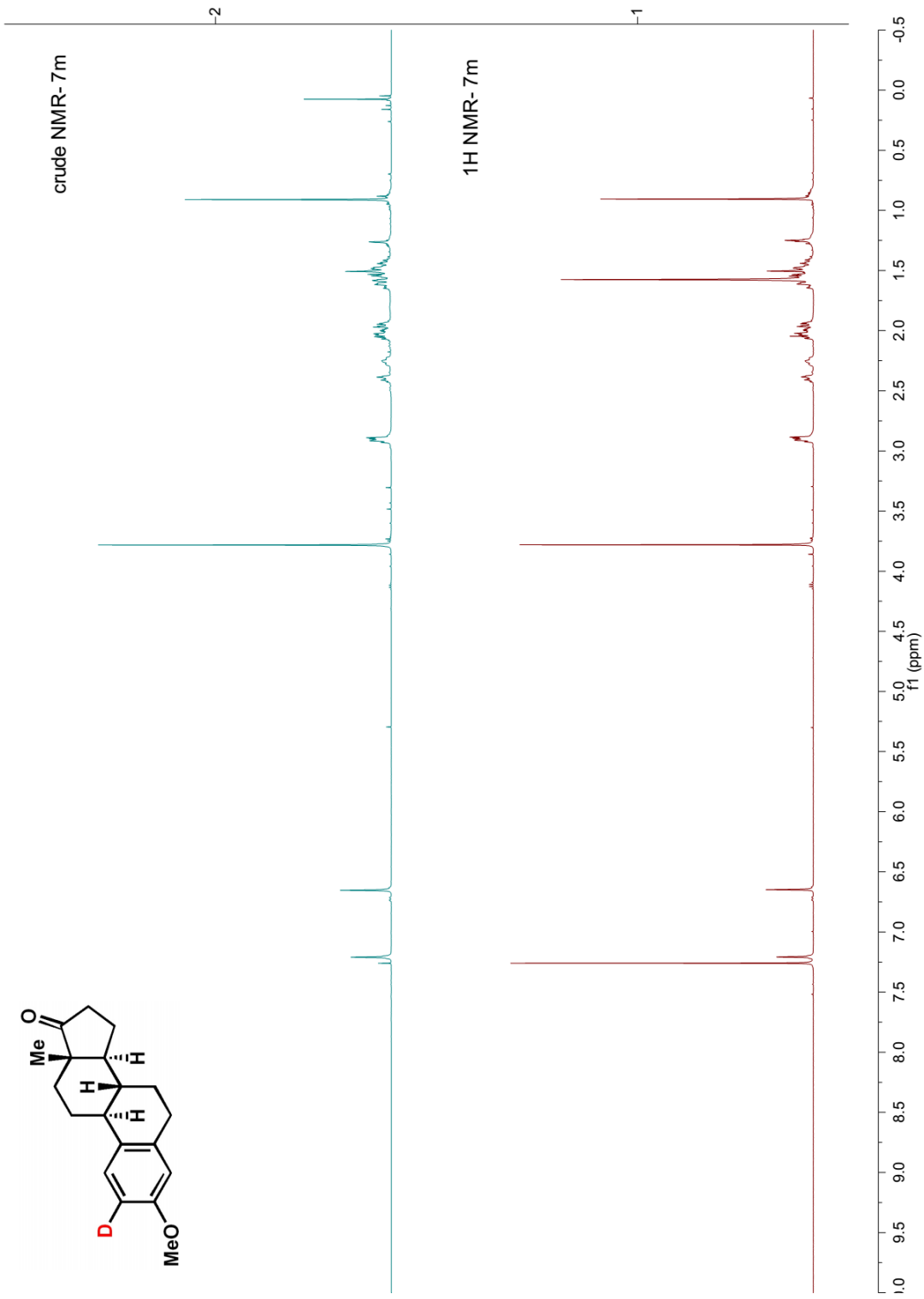

crude NMR- 7h
1H NMR- 7h
Cl
N
Me
N
Me
D
D
f1 (ppm)

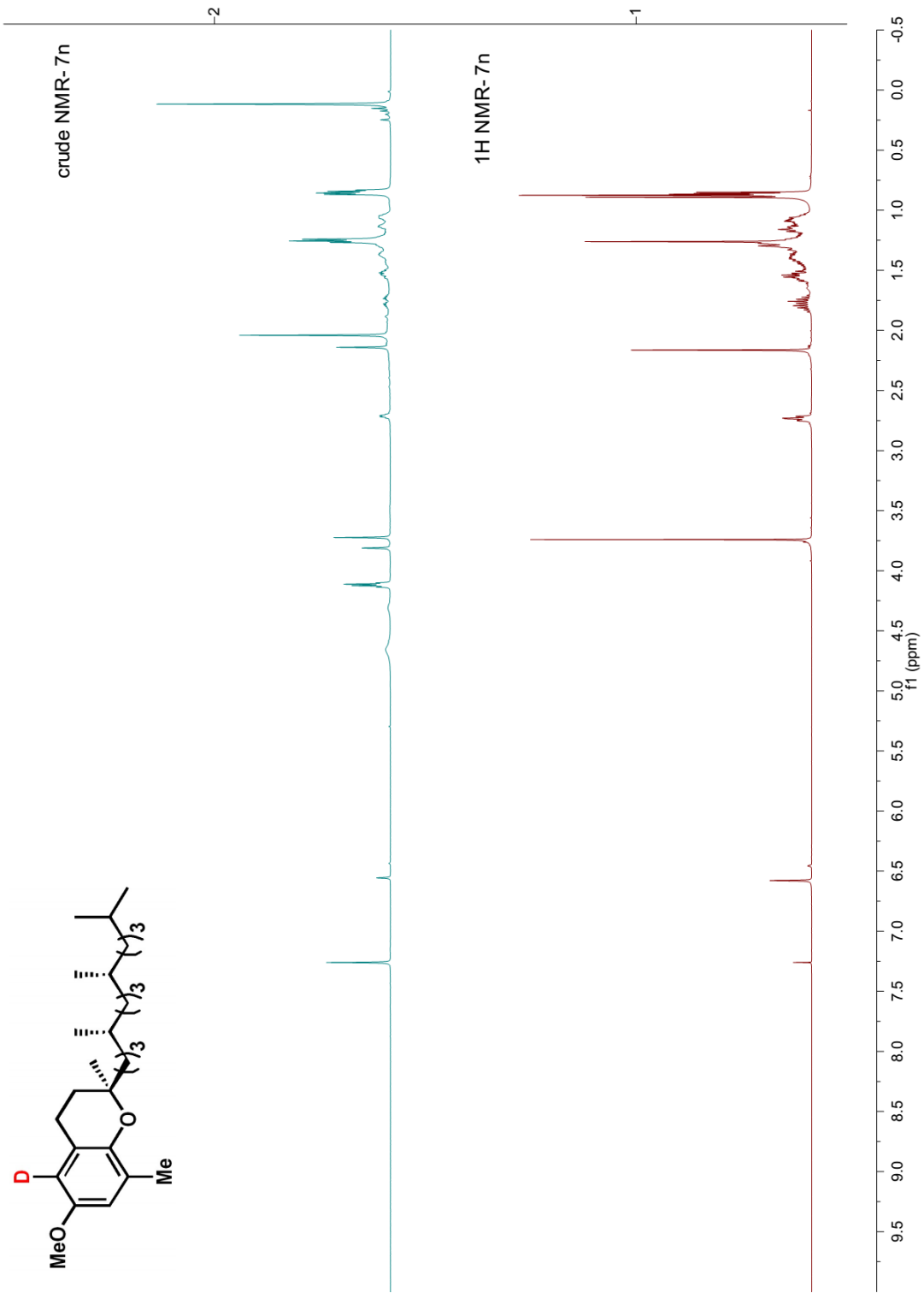

crude NMR- 7i
1H NMR- 7i
f1 (ppm)
Me
N
Me
O
D
D
Me
N
Me


crude NMR- 7j
1H NMR- 7j
f1 (ppm)
MeO
HO
Me
H
H
H
D
D
N
N
N
O


crude NMR- 7k
1H NMR- 7k
D
N
Me
H
H
H
MeO
f1 (ppm)


crude NMR- 7l
1H NMR- 7l
D
Me
H
H
H
MeO
f1 (ppm)


crude NMR- 7m
1H NMR- 7m
f1 (ppm)
Me
O
H
H
H
D
MeO


crude NMR- 7n
1H NMR- 7n
f1 (ppm)
D
MeO
Me
O